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Supporting Information for

Palladium-Catalyzed Enantioselective Decarboxylative Allylic Alkylation of Fully Substituted N-Acyl Indole-Derived Enol Carbonates.

Eric J. Alexy,[‡,a] Tyler J. Fulton,[‡,a] Haiming Zhang,*[,b] and Brian M. Stoltz*[,a]

[a]*Warren and Katharine Schlinger Laboratory of Chemistry and Chemical Engineering, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States*

[b]*Small Molecule Process Chemistry, Genentech, Inc., 1 DNA Way, South San Francisco, California 94080, United States*

zhang.haiming@gene.com

stoltz@caltech.edu

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Materials and Methods

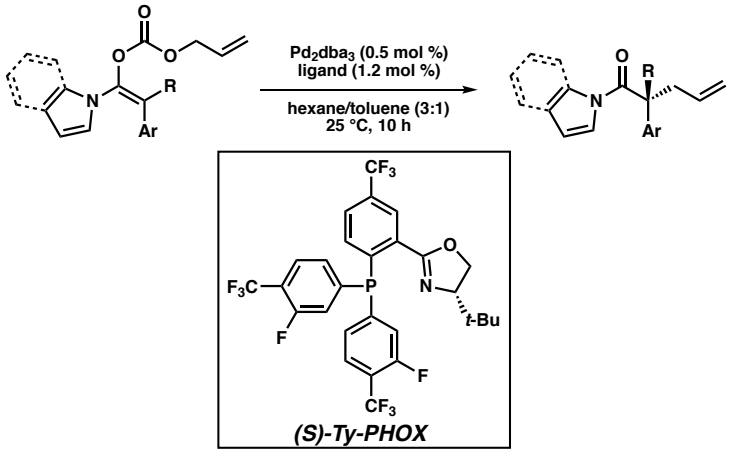
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 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 **2d** was determined by X-ray diffraction, and all other products are assigned by analogy.

Reagents were purchased from commercial sources and used as received unless otherwise stated. Ligand **L1** was prepared according to literature procedure.[2]

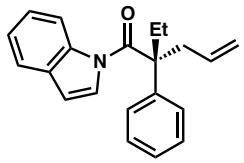
List of Abbreviations:

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

General Procedure for Pd-Catalyzed Allylic Alkylation Reactions



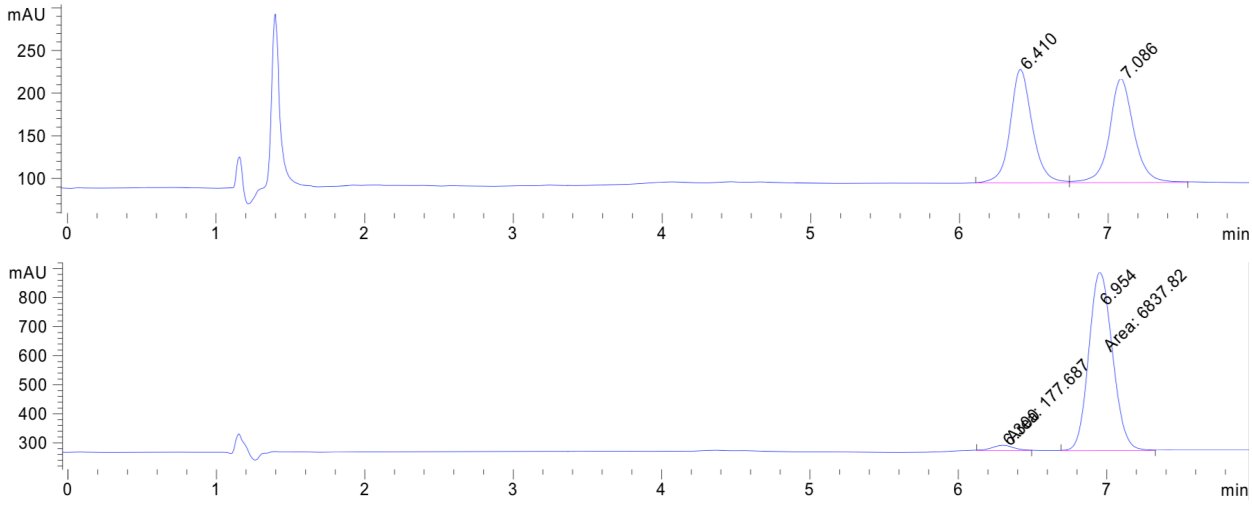
In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (1.8 mg/mL) and ***(S)-Ty-PHOX*** (2.8 mg/mL) in toluene was stirred for 30 min at 25 °C, then 0.5 mL of the resulting catalyst solution was added to a one dram vial containing allyl enol carbonate substrate (0.2 mmol) dissolved in hexane (1.5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



(*R*)-2-ethyl-1-(1*H*-indol-1-yl)-2-phenylpent-4-en-1-one (2a)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (64.8 mg, 99% yield); 95% ee, $[\alpha]_D^{25}$ –111.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.48–7.44 (m, 1H), 7.39–7.32 (m, 3H), 7.32–7.22 (m, 4H), 6.84 (d, *J* = 3.9 Hz, 1H), 6.26 (d, *J* = 3.8 Hz, 1H), 5.45 (dddd, *J* = 16.6, 10.2, 8.5, 6.2 Hz, 1H), 5.03–4.92 (m, 2H), 2.99 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.88 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.25 (qd, *J* = 7.4, 1.5 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 143.0, 136.5, 133.0, 129.5, 129.2, 127.3, 126.5, 126.1, 125.1, 123.7, 120.6, 119.0, 117.2, 108.2, 56.8, 40.5, 28.0, 8.4.; IR (Neat Film, NaCl) 3154, 3071, 2974, 2880, 1694, 1643, 1600, 1584, 1538, 1495, 1471, 1463, 1446, 1380, 1303, 1206, 1225, 1149, 1077, 1019, 1000, 920, 891, 820, 767, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}NO$ $[M+H]^+$: 304.1696, found 304.1691; SFC

Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 6.41, major = 6.95.



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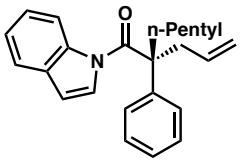
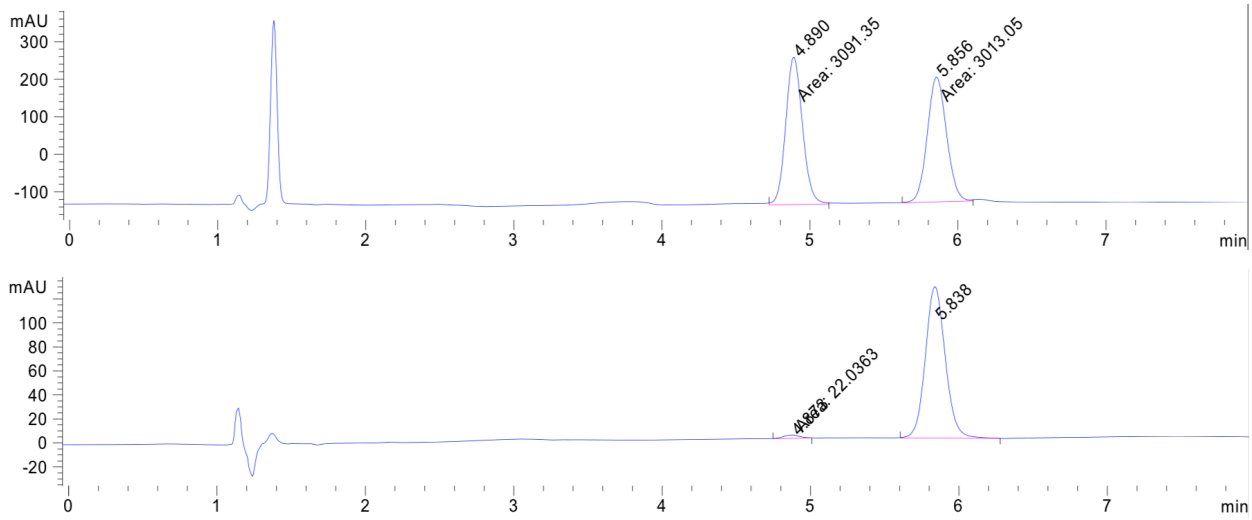


(*R*)-2-allyl-1-(1*H*-indol-1-yl)-2-phenylheptan-1-one (2b)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (68.4 mg, 99% yield); 96% ee, $[\alpha]_D^{25}$ –81.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (dq, *J* = 8.4, 0.8 Hz, 1H), 7.46 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.35 (ddt, *J* = 8.3, 5.3, 1.7 Hz, 3H), 7.30–7.22 (m, 4H), 6.85 (d, *J* = 3.9 Hz, 1H), 6.26 (dd, *J* = 3.8, 0.7 Hz, 1H), 5.44 (dddd, *J* = 16.6, 10.1, 8.5, 6.1 Hz, 1H), 5.03–4.90 (m, 2H), 3.00 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.88 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.25–2.11 (m, 2H), 1.35–1.24 (m, 1H), 1.21 (qd, *J* = 6.5, 6.0, 3.1 Hz, 4H), 1.10–0.98 (m, 1H), 0.81–0.75 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 143.2, 136.5, 133.2, 129.5, 129.2, 127.3, 126.4, 126.1, 125.1, 123.7, 120.6, 119.0, 117.3, 108.2, 56.4, 41.3, 35.0, 32.2, 23.4, 22.4, 14.0; IR (Neat Film, NaCl) 3071, 2954, 2928, 2859, 1696, 1449, 1304, 1204, 1078, 919, 750, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{28}NO$ $[M+H]^+$: 346.2165, found

346.2156; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.87, major = 5.84.



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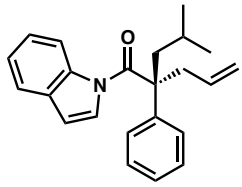
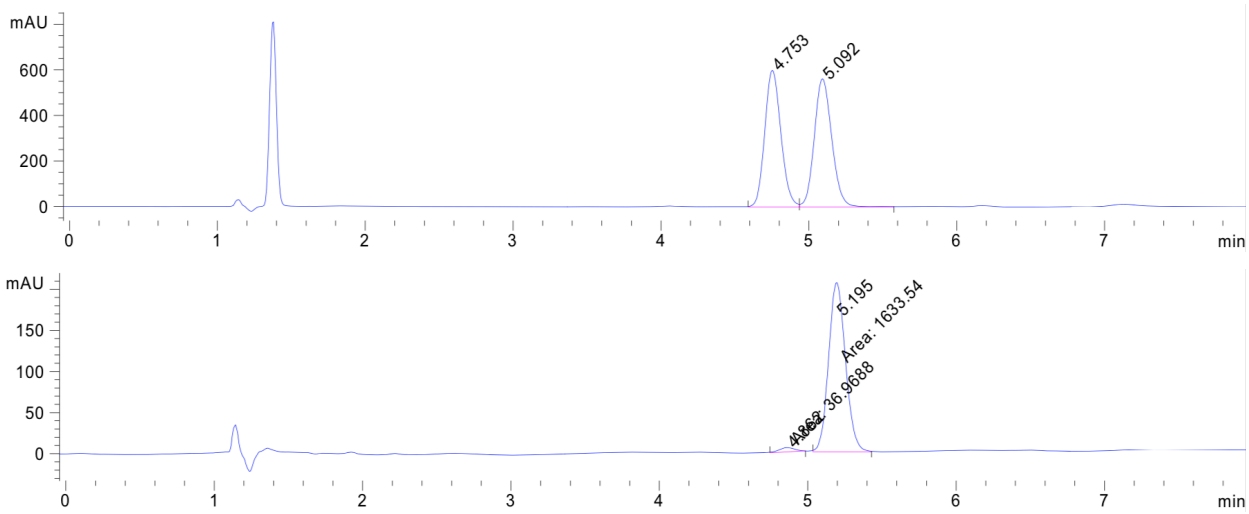


(*R*)-1-(1*H*-indol-1-yl)-2-isobutyl-2-phenylpent-4-en-1-one (2c)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (66.1 mg, 99% yield); 96% ee, $[\alpha]_D^{25}$ –109.1 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.62–8.52 (m, 1H), 7.49–7.43 (m, 1H), 7.39–7.32 (m, 3H), 7.30–7.21 (m, 4H), 6.87 (d, *J* = 3.8 Hz, 1H), 6.27 (d, *J* = 3.8 Hz, 1H), 5.42 (dddd, *J* = 16.5, 9.9, 8.7, 5.9 Hz, 1H), 5.04–4.89 (m, 2H), 3.13–3.01 (m, 1H), 2.91 (ddd, *J* = 14.2, 5.9, 1.5 Hz, 1H), 2.26 (dd, *J* = 14.1, 4.4 Hz, 1H), 2.10 (ddd, *J* = 14.1, 6.5, 1.1 Hz, 1H), 1.74 (ddt, *J* = 13.2, 11.0, 6.5 Hz, 1H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.62 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 143.3, 136.5, 133.3, 129.6, 129.2, 127.3, 126.4, 126.1, 125.2, 123.8, 120.6, 119.2, 117.3, 108.2, 56.1, 43.5, 42.2, 25.2, 24.1, 23.5; IR (Neat Film, NaCl) 3164, 3071, 3026, 2957, 2868, 1693, 1639, 1600, 1584, 1537, 1472, 1449, 1306, 1222, 1206, 1149, 1079, 919, 890, 767, 750, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2009, found 332.1998; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.86, major = 5.20.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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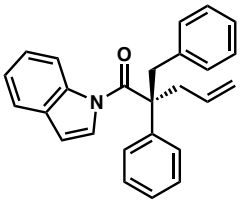
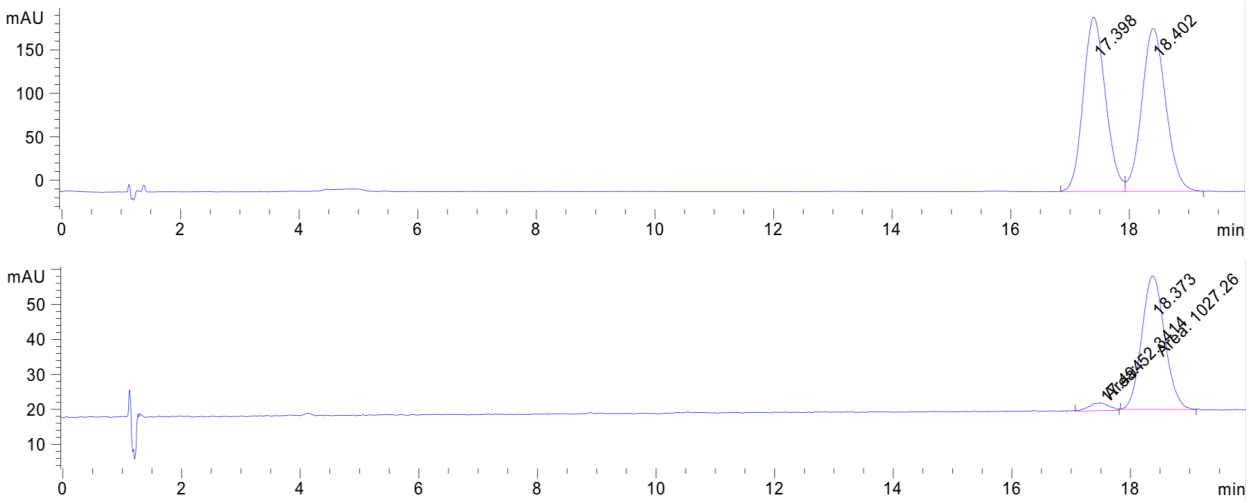
2	5.195	MM	0.1321	1633.53735	206.15324	97.7870



(*S*)-2-benzyl-1-(1*H*-indol-1-yl)-2-phenylpent-4-en-1-one (2d)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (70.5 mg, 96% yield); 90% ee, $[\alpha]_D^{25}$ +50.9 (*c* 0.65, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.54–8.50 (m, 1H), 7.48 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.38–7.29 (m, 4H), 7.29–7.23 (m, 1H), 7.18–7.11 (m, 3H), 7.06 (dd, *J* = 8.2, 6.9 Hz, 2H), 6.92 (d, *J* = 3.8 Hz, 1H), 6.60 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.32 (d, *J* = 3.9 Hz, 1H), 5.82–5.69 (m, 1H), 5.11–5.05 (m, 1H), 5.00–4.93 (m, 1H), 3.56 (d, *J* = 13.5 Hz, 1H), 3.42 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 142.4, 136.6, 136.3, 132.8, 130.8, 129.5, 129.1, 127.8, 127.6, 126.8, 126.7, 126.0, 125.2, 123.8, 120.6, 119.8, 117.3, 108.5, 57.8, 42.4, 39.0; IR (Neat Film, NaCl) 3062, 3028, 2926, 1694, 1601, 1584, 1537, 1495, 1449, 1328, 1305, 1203, 1078, 1019, 894, 751, 720, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{24}NO$ $[M+H]^+$: 366.1852, found 366.1855; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 235 nm, t_R (min): minor = 17.49, major = 18.37.



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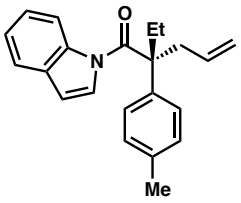
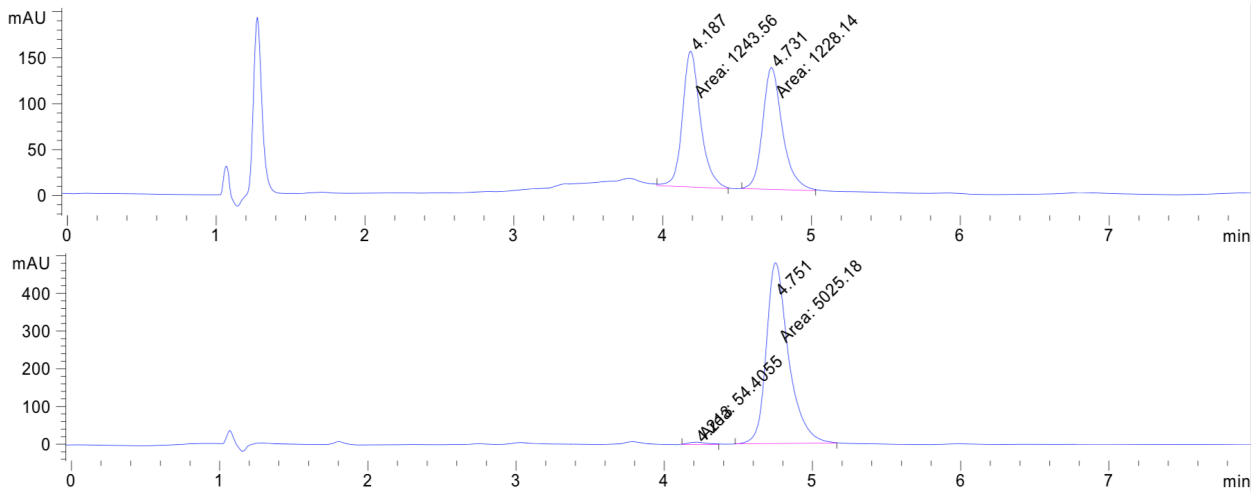


(*R*)-2-ethyl-1-(1*H*-indol-1-yl)-2-(*p*-tolyl)pent-4-en-1-one (2e)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (62.9 mg, 99% yield); 98% ee, $[\alpha]_D^{25}$ –112.1 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 8.4, 1.0 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.35 (ddt, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.26–7.21 (m, 1H), 7.15 (d, *J* = 1.0 Hz, 4H), 6.88 (dd, *J* = 3.9, 1.2 Hz, 1H), 6.27 (d, *J* = 3.8 Hz, 1H), 5.44 (dddd, *J* = 17.6, 10.9, 9.3, 6.6 Hz, 1H), 5.03–4.91 (m, 2H), 3.00–2.81 (m, 2H), 2.35 (s, 3H), 2.22 (q, *J* = 7.4 Hz, 2H), 0.80 (td, *J* = 7.4, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 139.9, 137.0, 136.5, 133.2, 129.9, 129.5, 126.3, 126.3, 125.0, 123.7, 120.5, 118.9, 117.2, 108.1, 56.4, 40.5, 28.0, 21.2, 8.4; IR (Neat Film, NaCl) 2973, 1695, 1640, 1585, 1537, 1514, 1472, 1450, 1380, 1321, 1304, 1224, 1206, 1105, 1077, 1020, 918, 893, 813, 768, 750 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1852, found 318.1848; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.21, major = 4.75.



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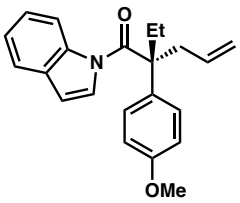
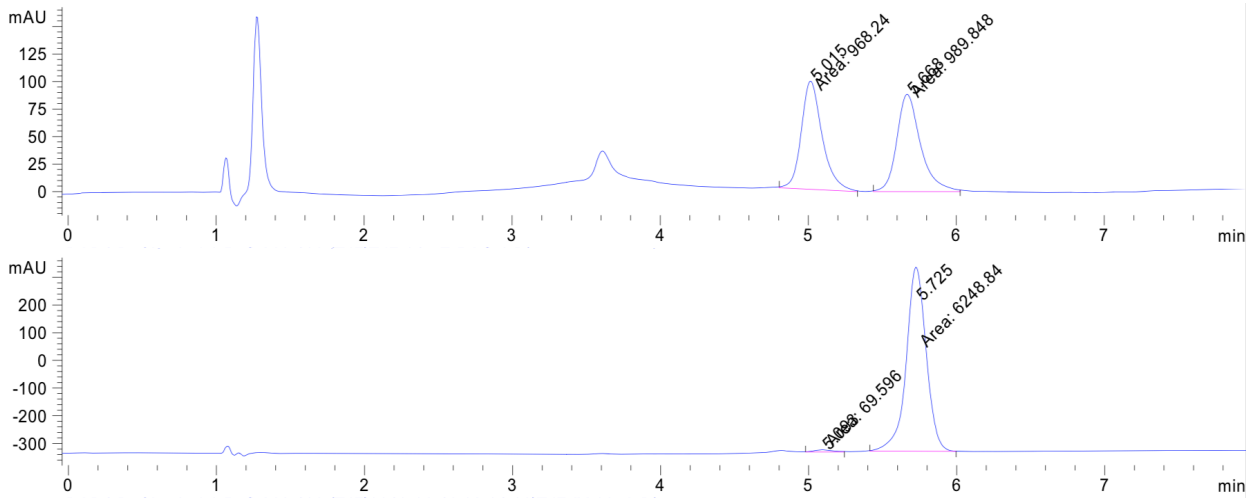


(*R*)-2-ethyl-1-(1*H*-indol-1-yl)-2-(4-methoxyphenyl)pent-4-en-1-one (2f)

Purified by column chromatography (10% Et_2O in hexanes) to provide an amorphous white solid (59.2mg, 89% yield); 98% ee, $[\alpha]_D^{25}$ –118.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (dq, *J* = 8.3, 0.8 Hz, 1H), 7.47 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.30–7.21 (m, 1H), 7.21–7.15 (m, 2H), 6.93–6.85 (m, 3H), 6.28 (dd, *J* = 3.9, 0.7 Hz, 1H), 5.45 (dddd, *J* = 16.6, 10.2, 8.5, 6.1 Hz, 1H), 5.04–4.90 (m, 2H), 3.81 (s, 3H), 2.96 (dd, *J* = 13.9, 8.5 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.21 (q, *J* = 7.4 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 158.6, 136.5, 134.9, 133.2, 129.5, 127.5, 126.3, 125.1, 123.7, 120.5, 118.9, 117.2, 114.5, 108.1, 56.1, 55.3, 40.5, 28.1, 8.4; IR (Neat Film, NaCl) 3163, 3073, 2973, 2837, 1694, 1640, 1609, 153, 1538, 1514, 1450, 1380, 1304, 1250, 1206, 1184, 1076, 1034, 919, 890, 819, 768, 750 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1802 found 334.1816; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 5.09, major = 5.73.



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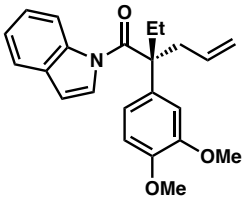
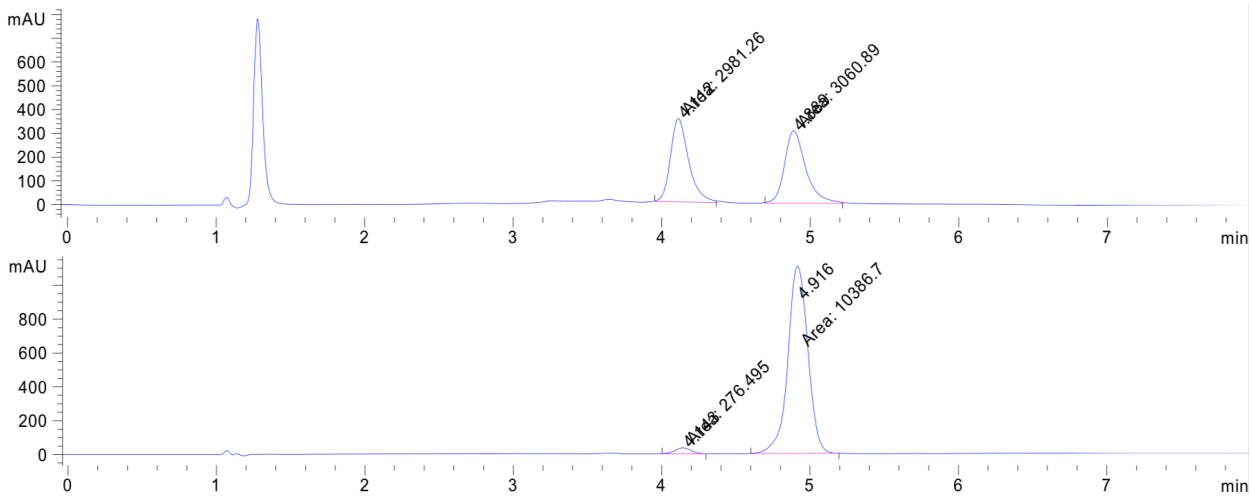
2	5.725	MM	0.1566	6248.83789	665.18439	98.8985

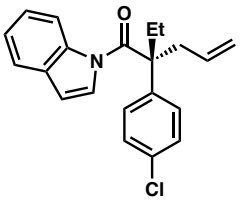


(*R*)-2-(3,4-dimethoxyphenyl)-2-ethyl-1-(1*H*-indol-1-yl)pent-4-en-1-one (2g)

Purified by column chromatography (20% Et_2O in hexanes) to provide an amorphous white solid (72.6 mg, 99% yield); 95% ee, $[\alpha]_D^{25}$ –96.6 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.53 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.40 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.33–7.28 (m, 1H), 6.98 (d, *J* = 3.8 Hz, 1H), 6.96–6.87 (m, 2H), 6.78 (d, *J* = 1.7 Hz, 1H), 6.34 (dt, *J* = 3.8, 0.8 Hz, 1H), 5.56–5.43 (m, 1H), 5.09–4.97 (m, 2H), 3.95 (s, 3H), 3.86 (s, 3H), 3.01 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.91 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.26 (q, *J* = 7.5 Hz, 2H), 0.91–0.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 149.5, 148.1, 136.4, 135.3, 133.1, 129.5, 126.1, 125.0, 123.7, 120.5, 118.9, 118.5, 117.0, 111.3, 109.6, 108.1, 56.3, 56.0, 55.9, 40.4, 28.0, 8.3. IR (Neat Film, NaCl) 3072, 2967, 2835, 1694, 1640, 1587, 1518, 1449, 1412, 1306, 1260, 1206, 1150, 1077, 1027, 917, 893, 803, 768, 751 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{26}NO_3$ $[M+H]^+$: 364.1907 found 364.1892; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.14, major = 4.92.

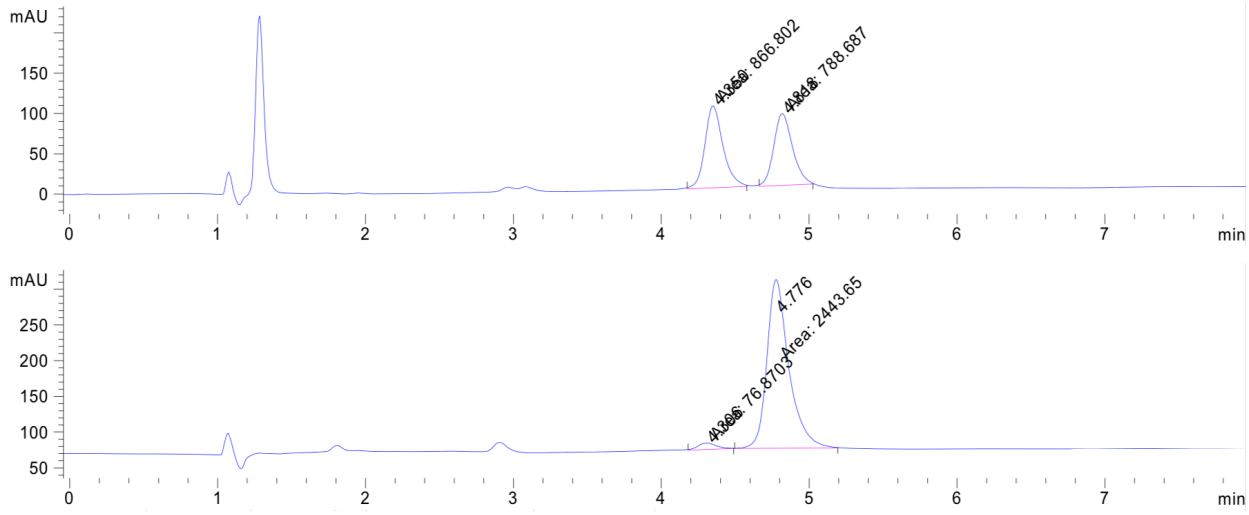


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.143	MM	0.1271	276.49503	36.25127	2.5930
2	4.916	MM	0.1563	1.03867e4	1107.40137	97.4070

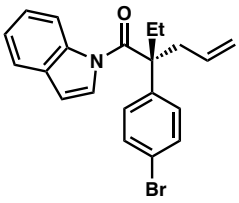


(*R*)-2-(4-chlorophenyl)-2-ethyl-1-(1*H*-indol-1-yl)pent-4-en-1-one (2h)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (68.2 mg, 99% yield); 94% ee, $[\alpha]_D^{25}$ –103.2 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.39–7.32 (m, 3H), 7.30–7.23 (m, 1H), 7.23–7.18 (m, 2H), 6.81 (dd, *J* = 3.9, 0.8 Hz, 1H), 6.31 (dd, *J* = 3.9, 0.7 Hz, 1H), 5.48–5.38 (m, 1H), 5.05–4.92 (m, 2H), 2.97 (ddt, *J* = 14.1, 8.4, 0.9 Hz, 1H), 2.84 (ddt, *J* = 13.9, 6.1, 1.3 Hz, 1H), 2.23 (q, *J* = 7.4 Hz, 2H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 141.6, 136.5, 133.3, 132.6, 129.5, 129.4, 127.9, 125.8, 125.3, 123.9, 120.7, 119.4, 117.2, 108.6, 56.5, 40.6, 28.1, 8.4; IR (Neat Film, NaCl) 3074, 2974, 2880, 1695, 1639, 1539, 1493, 1450, 1304, 1224, 1206, 1150, 1097, 1077, 1014, 920, 890, 815, 768, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{21}ClNO$ $[M+H]^+$: 338.1306 found 338.1291; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.31, major = 4.78.

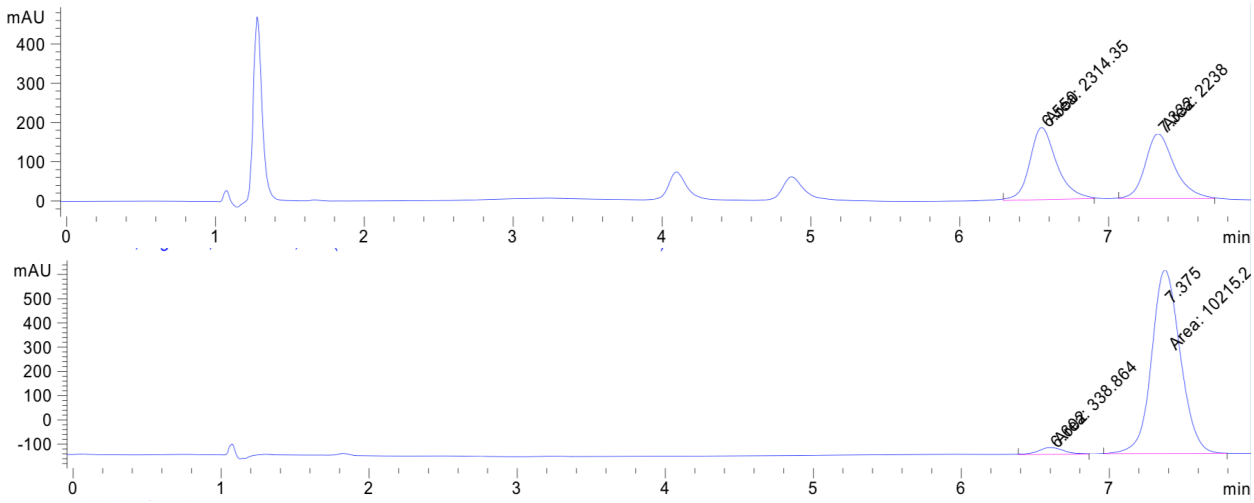


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.306	MM	0.1402	76.87028	9.13772	3.0498
2	4.776	MM	0.1723	2443.65186	236.30936	96.9502

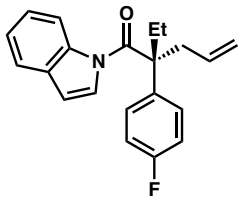


(*R*)-2-(4-bromophenyl)-2-ethyl-1-(1*H*-indol-1-yl)pent-4-en-1-one (2i)

Purified by column chromatography (5% Et_2O in hexanes) to provide as a white foam (75.2 mg, 98% yield); 94% ee, $[\alpha]_D^{25}$ –83.1 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.6 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.37 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.33–7.26 (m, 1H), 7.29–7.23 (m, 2H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.20 (dd, *J* = 3.9, 0.7 Hz, 1H), 5.44 (dddd, *J* = 16.6, 10.0, 8.5, 6.1 Hz, 1H), 5.05–4.89 (m, 2H), 3.02–2.91 (m, 1H), 2.87 (dd, *J* = 14.1, 6.2 Hz, 1H), 2.33–2.14 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 142.7, 135.2, 132.8, 131.3, 129.3, 127.9, 127.5, 127.2, 126.4, 123.2, 119.2, 118.5, 117.0, 107.3, 56.8, 40.3, 28.0, 8.3; IR (Neat Film, NaCl) 3162, 3065, 2974, 2879, 1698, 1639, 1598, 1574, 1534, 1496, 1443, 1364, 1304, 1266, 1218, 1199, 1080, 1032, 1000, 947, 920, 887, 822, 811, 762, 734, 718, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{21}BrNO$ $[M+H]^+$: 382.0801 found 382.0785; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 6.60, major = 7.38.

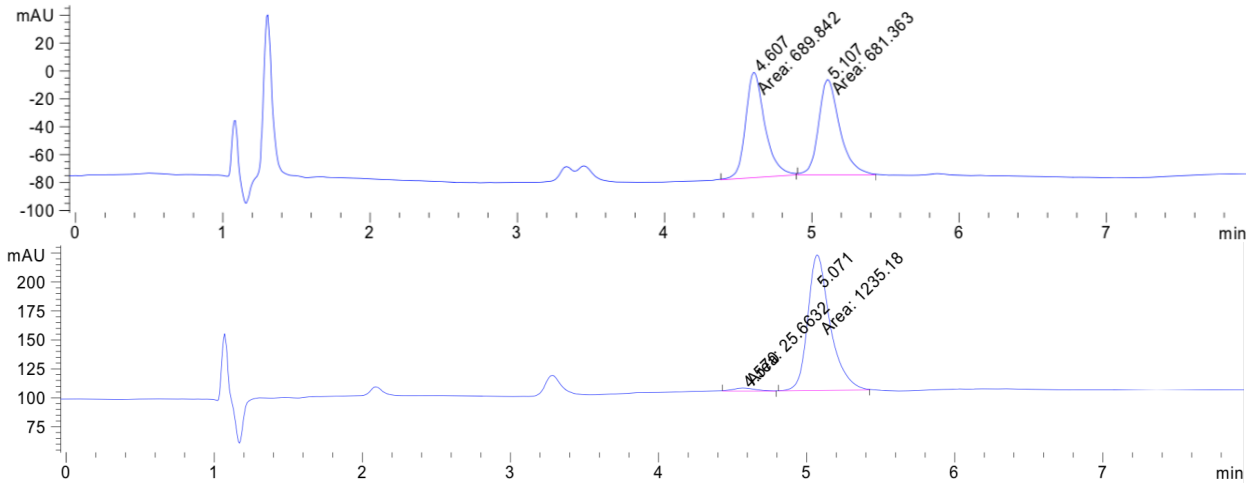


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.602	MM	0.1969	338.86377	28.68021	3.2107
2	7.375	MM	0.2247	1.02152e4	757.70929	96.7893

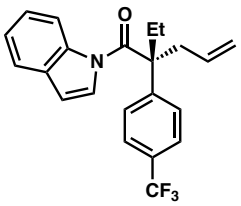


(*R*)-2-ethyl-2-(4-fluorophenyl)-1-(1*H*-indol-1-yl)pent-4-en-1-one (2j)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (62.1mg, 97% yield); 96% ee, $[\alpha]_D^{25}$ –97.3 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.27–7.19 (m, 3H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 3.9 Hz, 1H), 6.29 (d, *J* = 3.8 Hz, 1H), 5.42 (dtd, *J* = 16.8, 9.0, 6.3 Hz, 1H), 5.02–4.89 (m, 2H), 2.95 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.83 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.21 (q, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.82 (tt, *J* = 9.1, 4.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 162.0 (d, J_{C-F} = 246.9 Hz), 138.9 (d, J_{C-F} = 3.4 Hz), 136.5, 132.8, 129.5, 128.10 (d, J_{C-F} = 7.9 Hz), 125.9, 125.2, 123.9, 120.7, 119.3, 117.3, 116.1 (d, J_{C-F} = 21.4 Hz), 108.4, 56.3, 40.7, 28.2, 8.4; IR (Neat Film, NaCl) 3073, 2973, 1694, 1602, 1539, 1510, 1450, 1305, 1226, 1206, 1164, 1102, 1077, 1016, 920, 890, 822, 810, 768, 751 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{21}FNO$ $[M+H]^+$: 322.1602 found 322.1607; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.57, major = 5.07.

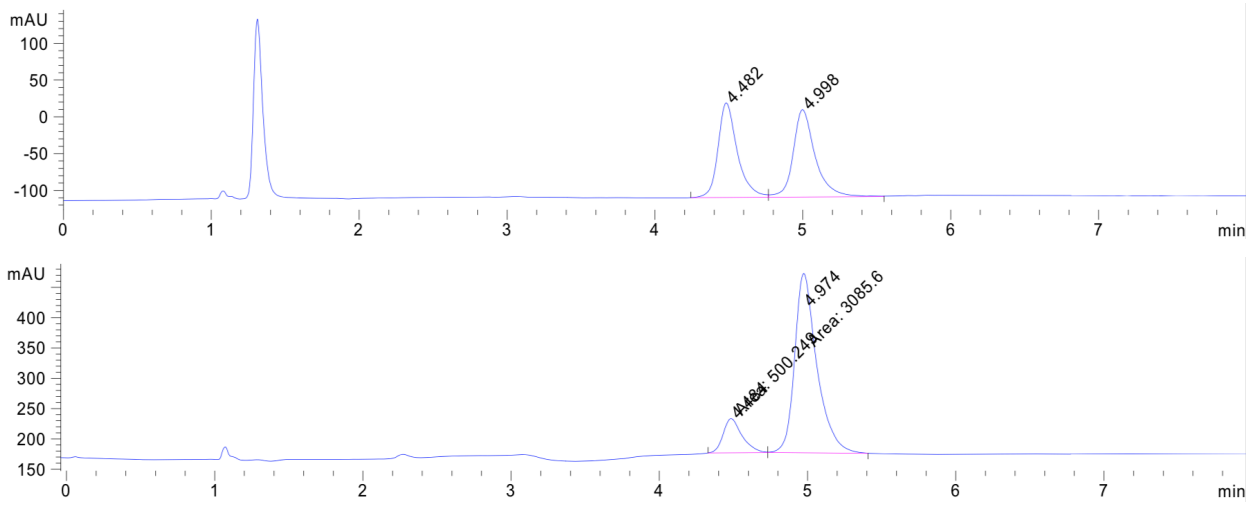


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.570	MM	0.1698	25.66317	2.51903	2.0354
2	5.071	MM	0.1756	1235.18494	117.20596	97.9646

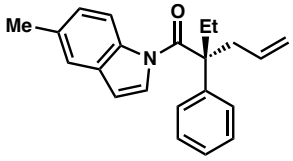


(*R*)-2-ethyl-1-(1*H*-indol-1-yl)-2-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (2k)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (73.0 mg, 98% yield); 70% ee, $[\alpha]_D^{25}$ –75.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.42–7.35 (m, 3H), 7.29–7.24 (m, 1H), 6.73 (d, *J* = 3.9 Hz, 1H), 6.31 (d, *J* = 3.9 Hz, 1H), 5.42 (dddd, *J* = 16.6, 10.2, 8.4, 6.2 Hz, 1H), 5.06–4.92 (m, 2H), 3.01 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.88 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.28 (qd, *J* = 7.3, 2.2 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 147.2 (overlapping), 136.5, 132.3, 129.6 (q, *J* = 32.7 Hz), 129.5, 127.0, 126.1 (q, *J* = 3.8 Hz), 125.5, 125.4, 124.1, 124.1 (q, *J* = 272.2 Hz), 120.7, 119.7, 117.3, 108.8, 56.9, 40.6, 28.1, 8.4. IR (Neat Film, NaCl) 3076, 2977, 2882, 1697, 1618, 1549, 1450, 1412, 1328, 1307, 1225, 1207, 1169, 1126, 1070, 1017, 922, 890, 843, 819, 768, 751 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}F_3NO$ $[M+H]^+$: 372.1570 found 372.1555; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.48, major = 4.97.

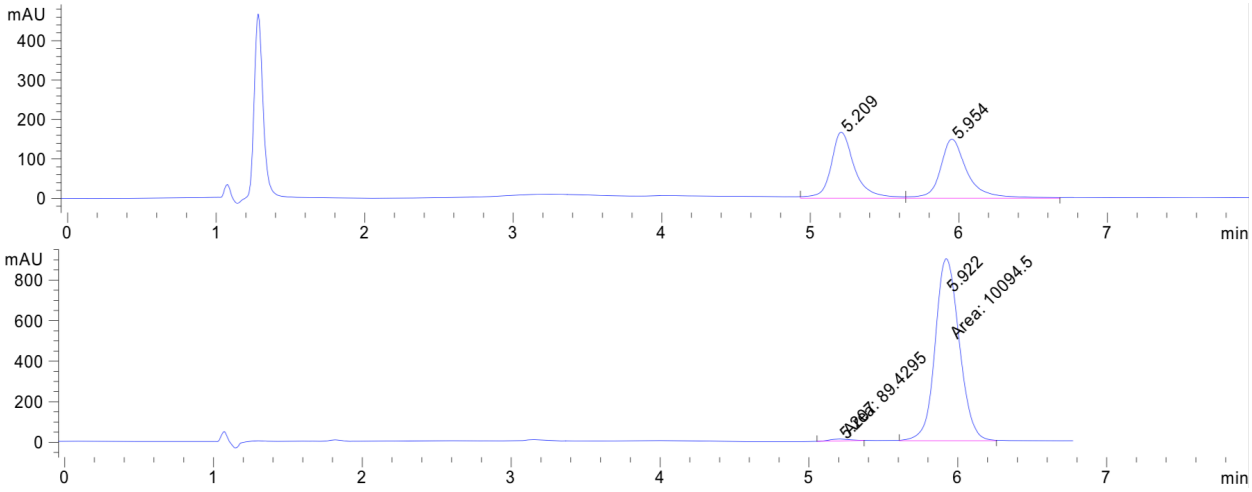


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.484	MM	0.1474	500.24872	56.57277	13.9506
2	4.974	MM	0.1737	3085.60352	296.06000	86.0494

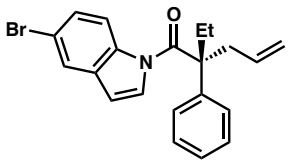


(*R*)-2-ethyl-1-(5-methyl-1*H*-indol-1-yl)-2-phenylpent-4-en-1-one (2l)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (63.4mg, 99% yield); 98% ee, $[\alpha]_D^{25}$ –111.7 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1H), 7.37–7.32 (m, 2H), 7.31–7.23 (m, 4H), 7.18 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.80 (d, *J* = 3.9 Hz, 1H), 6.19 (d, *J* = 3.8 Hz, 1H), 5.44 (dddd, *J* = 16.7, 10.3, 8.5, 6.2 Hz, 1H), 5.02–4.93 (m, 2H), 2.98 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.90–2.83 (m, 1H), 2.43 (s, 3H), 2.24 (qd, *J* = 7.4, 1.5 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 143.1, 134.7, 133.3, 133.1, 129.8, 129.1, 127.3, 126.5, 126.4, 126.1, 120.5, 118.9, 116.9, 108.0, 56.7, 40.5, 28.0, 21.4, 8.4; IR (Neat Film, NaCl) 3024, 2974, 2879, 1694, 1640, 1542, 1494, 1466, 1365, 1305, 1245, 1207, 1142, 1079, 1000, 919, 889, 830, 810, 766, 734, 716, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1852 found 318.1846; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 5.21, major = 5.92.

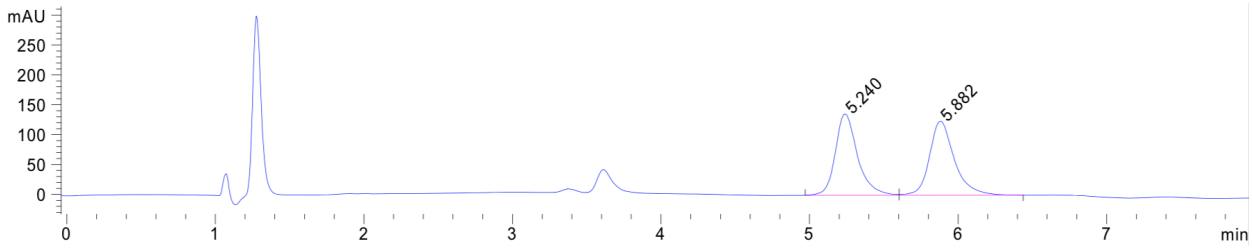


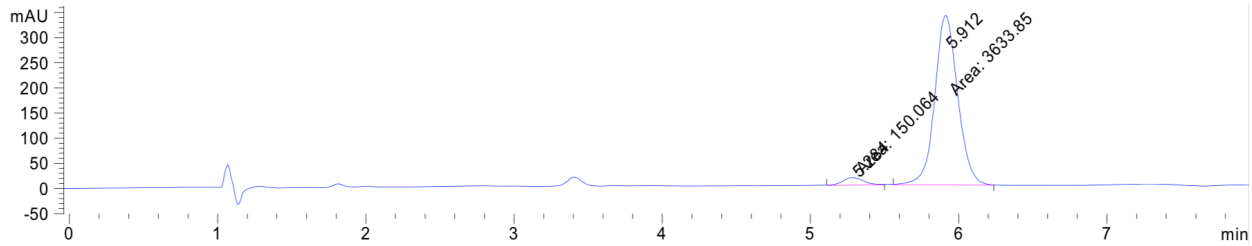
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.207	MM	0.1505	89.42949	9.90068	0.8781
2	5.922	MM	0.1873	1.00945e4	898.04572	99.1219



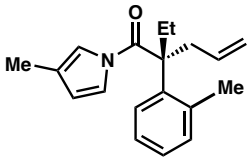
(*R*)-1-(5-bromo-1*H*-indol-1-yl)-2-ethyl-2-phenylpent-4-en-1-one (2m)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white foam (74.0 mg, 97% yield); 92% ee, $[\alpha]_D^{25}$ –112.5 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.51–7.45 (m, 3H), 7.36 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.28–7.24 (m, 1H), 7.17–7.11 (m, 2H), 6.81 (d, *J* = 3.9 Hz, 1H), 6.31 (dd, *J* = 3.9, 0.8 Hz, 1H), 5.43 (dddd, *J* = 16.6, 10.1, 8.4, 6.2 Hz, 1H), 5.03–4.92 (m, 2H), 2.96 (ddt, *J* = 14.0, 8.4, 1.0 Hz, 1H), 2.86–2.80 (m, 1H), 2.22 (q, *J* = 7.4 Hz, 2H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 142.1, 136.5, 132.6, 132.3, 129.5, 128.2, 125.8, 125.3, 123.9, 121.4, 120.7, 119.4, 117.2, 108.6, 56.5, 40.5, 28.0, 8.4; IR (Neat Film, NaCl) 3073, 2974, 1694, 1586, 1537, 1492, 1450, 1305, 1224, 1206, 1149, 1076, 1010, 920, 890, 814, 768, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{21}BrNO$ $[M+H]^+$: 382.0801 found 382.0811; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 5.28, major = 5.91.



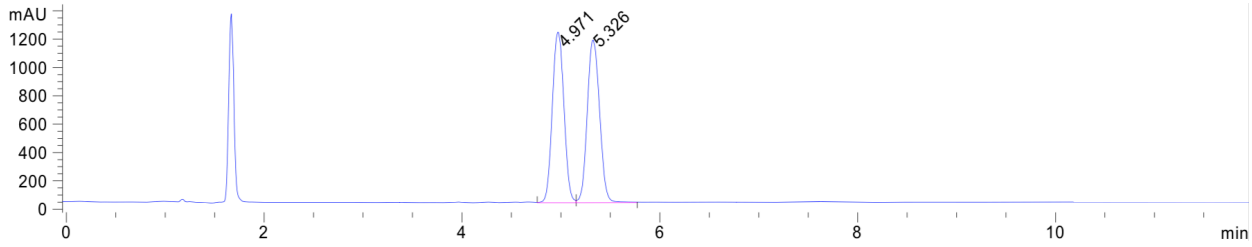


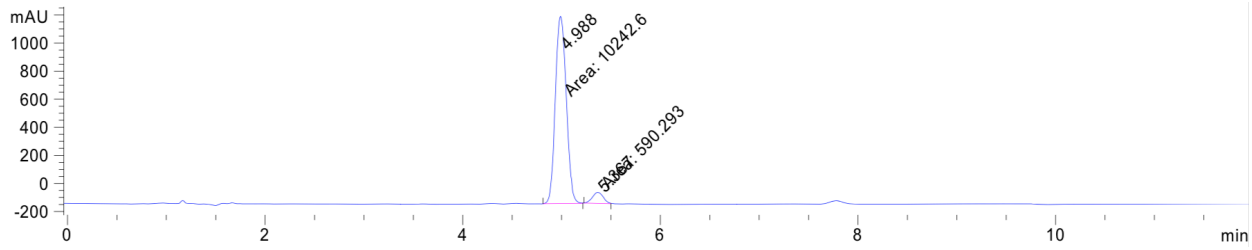
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.284	MM	0.1618	150.06354	15.45678	3.9658
2	5.912	MM	0.1796	3633.85181	337.18958	96.0342



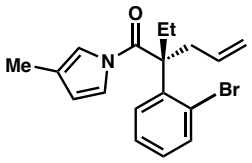
(*R*)-2-ethyl-1-(3-methyl-1*H*-pyrrol-1-yl)-2-(*o*-tolyl)pent-4-en-1-one (2n)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (56.1 mg, 99% yield); 89% ee, $[\alpha]_D^{25}$ –87.4 (*c* 1.0, $CHCl_3$); Note: Rotameric species were observed for this compound, thus the ^1H NMR spectrum was recorded at elevated temperature (50 ºC): ^1H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 7.37 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.30–7.21 (m, 1H), 7.18 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 10.9 Hz, 2H), 5.84 (dt, *J* = 3.2, 1.5 Hz, 1H), 5.39 (s, 1H), 5.05–4.90 (m, 2H), 2.90 (d, *J* = 7.3 Hz, 2H), 2.26 (dd, *J* = 13.1, 6.6 Hz, 1H), 2.14 (d, *J* = 11.3 Hz, 2H), 2.13 (s, 2H), 1.91 (d, *J* = 1.3 Hz, 3H), 0.77 (s, 3H); Note: Rotameric species were observed for this compound, thus the ^{13}C NMR spectrum contains broad peaks: ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 140.8, 136.8, 133.3, 132.7, 127.3, 126.4, 126.1, 122.5, 120.4, 118.8, 117.4, 114.4, 54.6, 37.8, 28.0, 20.3, 12.0, 8.4; IR (Neat Film, NaCl) 3143, 3073, 2976, 2880, 1699, 1639, 1490, 1459, 1490, 1459, 1389, 1337, 1309, 1199, 1134, 1080, 1068,990, 918, 893, 827, 773, 740 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852 found 282.1843; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralpak OD-H column, λ = 210 nm, t_R (min): minor = 4.99, major = 5.37.



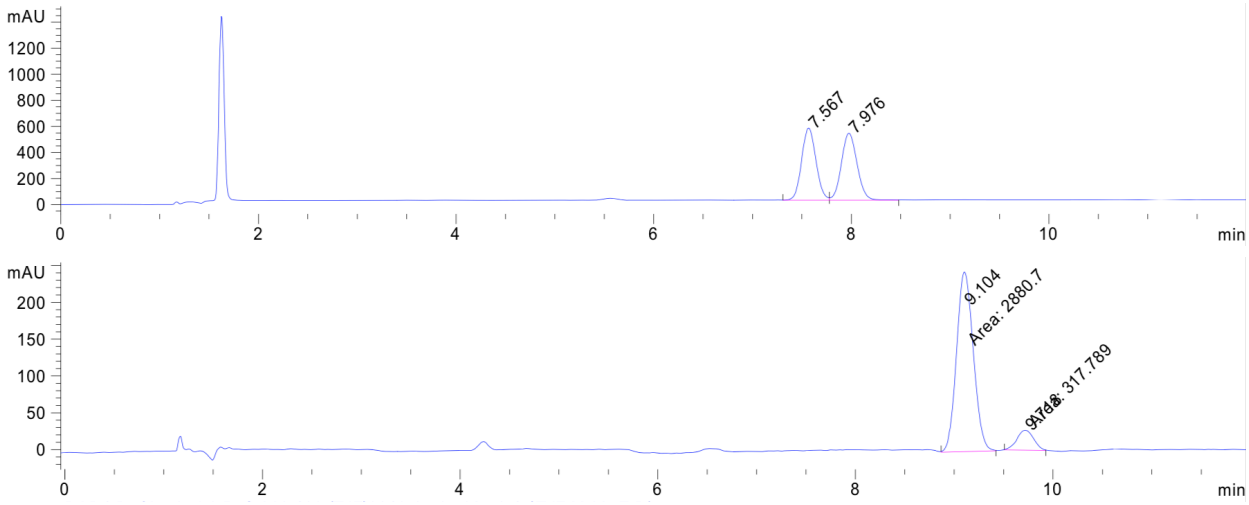


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.988	MM	0.1279	1.02426e4	1334.22021	94.5509
2	5.367	MM	0.1256	590.29285	78.34911	5.4491



(*R*)-2-(2-bromophenyl)-2-ethyl-1-(3-methyl-1*H*-pyrrol-1-yl)pent-4-en-1-one (2o)

Purified by column chromatography (5% Et_2O in hexanes) to provide an amorphous white solid (60.1 mg, 87% yield); 80% ee, $[\alpha]_D^{25}$ –80.9 (*c* 1.0, $CHCl_3$); Note: Rotameric species were observed for this compound, thus the ^{1}H NMR spectrum was recorded at elevated temperature (50 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.43–7.36 (m, 1H), 7.16 (td, *J* = 7.5, 1.6 Hz, 1H), 6.74 (d, *J* = 9.1 Hz, 2H), 5.86 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.46–5.24 (m, 1H), 5.04–4.92 (m, 2H), 3.14 (dd, *J* = 14.4, 6.3 Hz, 1H), 3.01–2.85 (m, 1H), 2.46–2.33 (m, 1H), 2.19–2.05 (m, 1H), 1.92 (s, 3H), 0.80 (s, 3H); Note: Rotameric species were observed for this compound, thus the ^{13}C NMR spectrum contains broad peaks: ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 141.8, 135.3, 132.9, 129.0, 128.5, 127.8, 124.2, 122.5, 120.2, 119.1, 117.4, 114.4, 55.8, 36.5, 28.0, 12.1, 8.8; IR (Neat Film, NaCl) 2977, 1704, 1485, 1470, 1390, 1309, 1201, 1134, 1068, 1025, 919, 828, 769, 741 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{21}BrNO$ $[M+H]^+$: 346.0801 found 346.0790; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralpak OD-H column, λ = 210 nm, t_R (min): minor = 9.10, major = 9.72.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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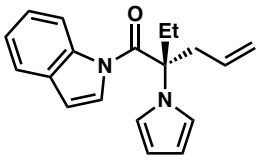
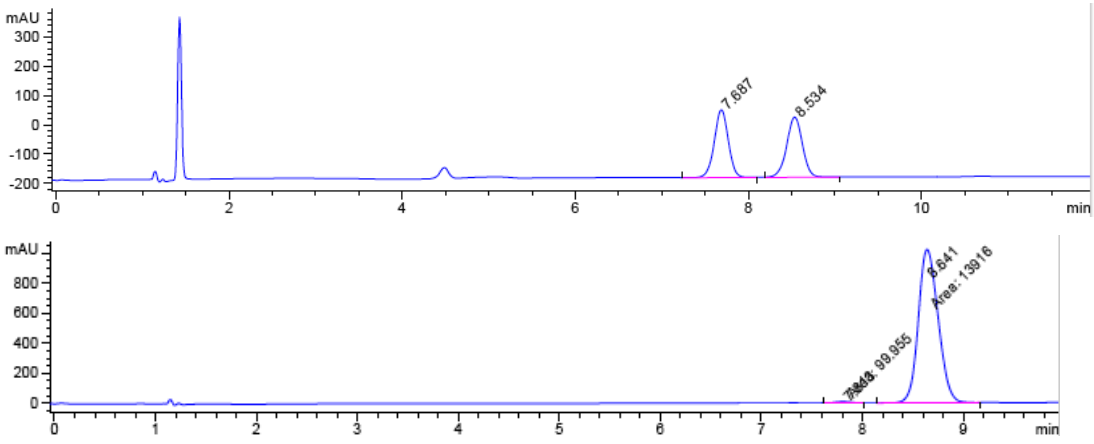
2	9.718	MM	0.1944	317.78879	27.24121	9.9356



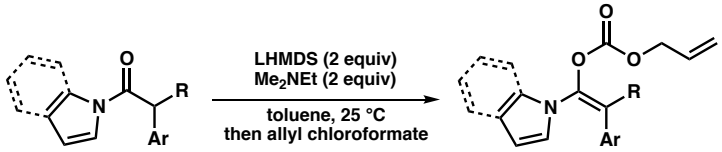
(*S*)-2-ethyl-1-(1*H*-indol-1-yl)-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2p)

Purified by column chromatography (2% Et_2O in hexanes) to provide colorless oil (56.8 mg, 97% yield); 99% ee, $[a]_D^{25}$ 104.2 (*c* 0.25, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.49 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.36 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.29–7.25 (m, 1H), 6.80 (t, *J* = 2.2 Hz, 2H), 6.39–6.18 (m, 4H), 5.38 (dddd, *J* = 16.8, 10.2, 8.0, 6.5 Hz, 1H), 5.17–4.91 (m, 2H), 3.10–2.95 (m, 2H), 2.45–2.22 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 136.8, 131.2, 129.7, 125.3, 124.6, 124.1, 120.7, 120.23, 118.6, 117.1, 109.9, 69.6, 40.4, 28.4, 8.1; IR (Neat Film, NaCl) 3156, 2978, 1697, 1538, 1450, 1381, 1356, 1309, 1227, 1204, 1152, 1079, 926, 880, 821, 751, 723 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1648 found 293.1641; SFC Conditions: 6% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 7.81, major = 8.64.

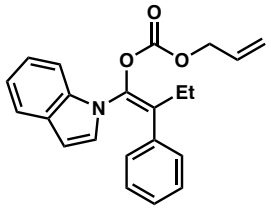


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.813	MM	0.1753	99.95499	9.50271	0.7132
2	8.641	MM	0.2264	1.39160e4	1024.34534	99.2868

Selective Enolization of *N*-Acyl Substrates

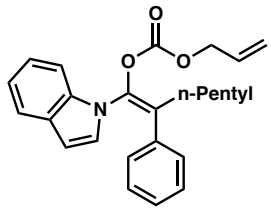


To a flame-dried flask was added LHMDS (335 mg, 2 mmol) followed by toluene (3.0 mL) and N,N-dimethylethylamine (0.213 mL, 2 mmol), and the resulting mixture stirred at 25 °C for 5 min. A solution of *N*-acyl indole (1 mmol) in toluene (2.0 mL) was then added, and the reaction stirred at 25 °C for an additional 2 hours. 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 min). 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 ^1H NMR and is >95:5 unless stated otherwise.



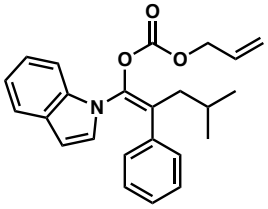
(*E*)-1-(1*H*-indol-1-yl)-2-phenylbut-1-en-1-yl allyl carbonate (1a)

Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a colorless oil (2.08 g, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.43 (m, 2H), 7.24–7.18 (m, 1H), 7.15–7.06 (m, 4H), 7.02–6.94 (m, 2H), 6.89 (d, *J* = 3.3 Hz, 1H), 6.35 (dd, *J* = 0.9, 3.4 Hz, 1H), 5.88 (ddt, *J* = 5.8, 10.4, 17.1 Hz, 1H), 5.37–5.23 (m, 2H), 4.61 (dt, *J* = 1.4, 5.8 Hz, 2H), 2.68 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 136.2, 135.0, 130.8, 130.2, 129.0, 128.4, 128.2, 127.5, 127.5, 122.6, 120.7, 119.4, 111.2, 103.9, 69.3, 24.9, 12.6; IR (Neat Film, NaCl) 3056, 2974, 1766, 1682, 1519, 1456, 1333, 1259, 1238, 1209, 1143, 1119, 1094, 1042, 968, 946, 913, 765, 743, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1594, found 348.1588.



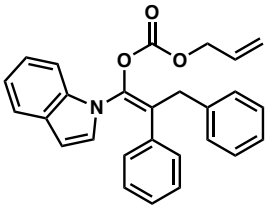
(*E*)-1-(1*H*-indol-1-yl)-2-phenylhept-1-en-1-yl allyl carbonate (1b)

Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a colorless oil (337.6 mg, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.45 (m, 2H), 7.23–7.16 (m, 1H), 7.14–7.05 (m, 4H), 6.98–6.91 (m, 2H), 6.89–6.84 (m, 1H), 6.36–6.30 (m, 1H), 5.94–5.81 (m, 1H), 5.36–5.22 (m, 2H), 4.60 (dq, *J* = 5.8, 1.4 Hz, 2H), 2.70–2.60 (m, 2H), 1.49–1.26 (m, 6H), 0.89 (td, *J* = 7.1, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 136.4, 136.3, 135.4, 130.9, 129.1, 129.0, 128.4, 128.2, 127.5, 127.5, 122.6, 120.7, 120.7, 119.4, 111.2, 103.9, 69.3, 31.5, 31.4, 27.3, 22.4, 14.1; IR (Neat Film, NaCl) 3055, 2956, 2929, 2860, 2363, 2340, 1765, 1684, 1457, 1332, 1242, 1211, 1142, 1118, 948, 764, 742, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{28}NO_3$ $[M+H]^+$: 390.2064, found 390.2078.



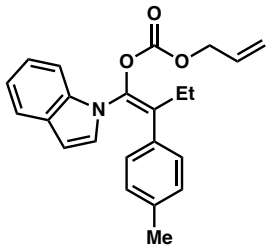
(*E*)-1-(1*H*-indol-1-yl)-4-methyl-2-phenylpent-1-en-1-yl allyl carbonate (1c)

Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (327.6 mg, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (ddd, *J* = 7.4, 5.8, 1.0 Hz, 2H), 7.21 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.15–7.08 (m, 4H), 6.99–6.91 (m, 2H), 6.84 (d, *J* = 3.3 Hz, 1H), 6.33 (d, *J* = 3.3 Hz, 1H), 5.88 (ddt, *J* = 17.3, 10.5, 5.8 Hz, 1H), 5.32 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.3, 1.3 Hz, 1H), 4.60 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.56 (d, *J* = 7.3 Hz, 2H), 1.62 (hept, *J* = 6.8 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.5, 136.3, 136.1, 130.9, 129.2, 128.4, 128.2, 128.0, 127.5, 127.4, 122.6, 120.7, 120.7, 119.4, 111.2, 103.8, 69.3, 40.2, 26.5, 22.4; IR (Neat Film, NaCl) 3057, 3031, 2957, 2869, 1766, 1682, 1519, 1456, 1331, 1246, 1331, 1246, 1209, 1144, 1118, 1046, 960, 767, 743, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907, found 376.1902.



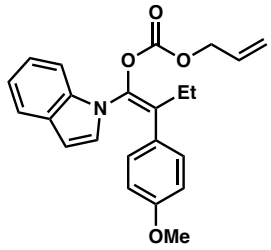
(*E*)-1-(1*H*-indol-1-yl)-2,3-diphenylprop-1-en-1-yl allyl carbonate (1d)

Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a yellow oil (377.6 mg, 92% yield); ^{1}H NMR (500 MHz, $CHCl_3$) δ 7.58–7.49 (m, 2H), 7.34–7.25 (m, 4H), 7.26–7.18 (m, 2H), 7.14 (tt, *J* = 7.1, 0.9 Hz, 1H), 7.07–6.99 (m, 3H), 6.95 (m, 1H), 6.94–6.87 (m, 2H), 6.39 (dt, *J* = 3.4, 0.8 Hz, 1H), 5.91–5.79 (m, 1H), 5.35–5.22 (m, 2H), 4.58 (dt, *J* = 5.9, 1.3 Hz, 2H), 4.03 (s, 2H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 152.4, 138.0, 136.5, 136.1, 136.1, 130.7, 128.9, 128.8, 128.5, 128.4, 128.1, 127.7, 127.5, 126.6, 126.4, 122.7, 120.9, 120.8, 119.4, 111.3, 104.2, 69.4, 37.7; IR (Neat Film, NaCl) 3059, 3028, 1766, 1678, 1602, 1519, 1495, 1456, 1384, 1364, 1333, 1243, 1214, 1142, 1117, 967, 945 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{27}H_{24}NO_3$ $[M+H]^+$: 410.1751, found 410.1749.



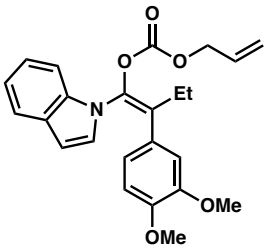
(*E*)-1-(1*H*-indol-1-yl)-2-(*p*-tolyl)but-1-en-1-yl allyl carbonate (1e)

Purified by column chromatography (6% Et_2O in hexanes) to provide the desired product as a yellow oil (268.7 mg, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.42 (m, 2H), 7.19 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.92–6.80 (m, 5H), 6.35 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.41–5.18 (m, 2H), 4.59 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 137.2, 136.3, 134.8, 133.2, 130.9, 130.3, 129.2, 129.0, 128.5, 127.5, 122.6, 120.8, 120.7, 119.6, 111.4, 103.8, 69.4, 25.0, 21.2, 12.7; IR (Neat Film, NaCl) 1764, 1457, 1333, 1258, 1238, 1209, 1143, 1120, 945, 818, 743 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1751, found 362.1741.



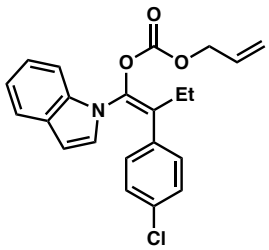
(*E*)-1-(1*H*-indol-1-yl)-2-(4-methoxyphenyl)but-1-en-1-yl allyl carbonate (1f)

Purified by column chromatography (10% Et_2O in hexanes) to provide the desired product as a yellow oil (245.6 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 7.8, 1.2, 0.8 Hz, 1H), 7.45 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.19 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.92–6.82 (m, 3H), 6.67– 6.57 (m, 2H), 6.36 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.37–5.19 (m, 2H), 4.59 (d, *J* = 5.8 Hz, 2H), 3.68 (s, 3H), 2.63 (q, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.9, 136.3, 134.6, 131.0, 129.9, 129.2, 128.8, 128.5, 128.3, 122.7, 120.8, 120.8, 119.6, 113.7, 111.4, 103.9, 69.5, 55.2, 25.0, 12.8; IR (Neat Film, NaCl) 1764, 1609, 1513, 1456, 1293, 1247, 1209, 1142, 1121, 1038, 831, 744 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1700, found 378.1690.



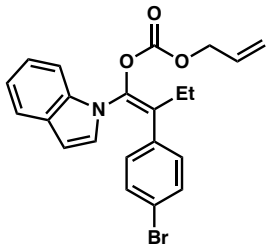
(*E*)-allyl (2-(3,4-dimethoxyphenyl)-1-(1*H*-indol-1-yl)but-1-en-1-yl) carbonate (1g)

Purified by column chromatography (20% Et_2O in hexanes) to provide the desired product as a colorless oil (262.1 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.48 (m, 2H), 7.21 (ddd, *J* = 1.3, 7.1, 8.3 Hz, 1H), 7.11 (td, *J* = 1.1, 7.5 Hz, 1H), 6.92 (t, *J* = 2.2 Hz, 1H), 6.71 (dt, *J* = 1.9, 8.3 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.38 (dt, *J* = 1.2, 3.5 Hz, 1H), 6.17 (t, *J* = 1.8 Hz, 1H), 5.89 (ddt, *J* = 5.8, 10.3, 17.1 Hz, 1H), 5.41–5.19 (m, 2H), 4.62 (dt, *J* = 1.4, 5.8 Hz, 2H), 3.77 (s, 3H), 3.23 (s, 3H), 2.68 (qd, *J* = 2.4, 7.6 Hz, 2H), 1.12 (td, *J* = 2.2, 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 148.4, 148.3, 136.6, 134.5, 130.9, 130.6, 129.2, 128.4, 128.4, 122.7, 120.8, 120.8, 119.7, 119.6, 111.1, 110.7, 110.6, 104.0, 69.4, 55.7, 55.2, 24.7, 12.9; IR (Neat Film, NaCl) 1763, 1518, 1456, 1262, 1242, 1208, 1139, 1116, 1026, 946, 766, 744 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}NO_5$ $[M+H]^+$: 408.1805, found 408.1817.



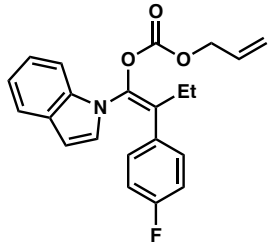
(*E*)-allyl (2-(4-chlorophenyl)-1-(1*H*-indol-1-yl)but-1-en-1-yl) carbonate (1h)

Purified by column chromatography (8% Et_2O in hexanes) to provide the desired product as a light yellow oil (356.3 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.48 (m, 1H), 7.43 (dq, *J* = 0.9, 8.2 Hz, 1H), 7.19 (ddd, *J* = 1.2, 7.1, 8.2 Hz, 1H), 7.11 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H), 7.09–7.03 (m, 2H), 6.92–6.82 (m, 3H), 6.37 (dd, *J* = 0.9, 3.4 Hz, 1H), 5.86 (ddt, *J* = 5.8, 10.5, 17.2 Hz, 1H), 5.36–5.23 (m, 2H), 4.59 (dt, *J* = 1.3, 5.8 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.2, 135.4, 134.8, 133.4, 130.8, 129.2, 129.0, 128.9, 128.6, 128.5, 122.9, 121.0, 120.9, 119.8, 111.2, 104.4, 69.6, 24.9, 12.7; IR (Neat Film, NaCl) 1765, 1679, 1456, 1333, 1256, 1238, 1209, 1144, 1120, 1096, 945, 827, 743 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}ClNO_3$ $[M+H]^+$: 382.1204, found 382.1201.



(*E*)-allyl (2-(4-bromophenyl)-1-(1*H*-indol-1-yl)but-1-en-1-yl) carbonate (1i)

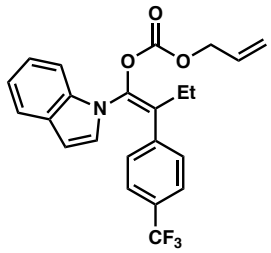
Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as an amorphous white solid (341.0 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 1H), 7.43 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.24–7.17 (m, 3H), 7.14–7.09 (m, 1H), 6.86 (d, *J* = 3.4 Hz, 1H), 6.86–6.78 (m, 2H), 6.37 (d, *J* = 3.1 Hz, 1H), 5.86 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H), 5.36–5.23 (m, 2H), 4.59 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.1, 135.3, 135.2, 131.5, 130.8, 129.3, 129.2, 128.8, 128.5, 122.8, 121.6, 121.0, 120.9, 119.7, 111.2, 104.4, 69.5, 24.8, 12.7; IR (Neat Film, NaCl) 3053, 3032, 2974, 2937, 2876, 2248, 1899, 1766, 1681, 1588, 1519, 1488, 1455, 1385, 1364, 1333, 1238, 1209, 1144, 1120, 945, 824, 766, 743 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}BrNO_3$ $[M+H]^+$: 426.0699, found 426.0696.



(*E*)-allyl (2-(4-fluorophenyl)-1-(1*H*-indol-1-yl)but-1-en-1-yl) carbonate (1j)

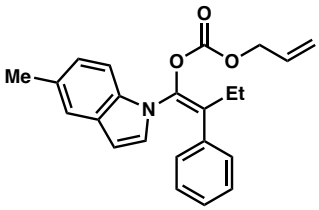
Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a colorless oil (312.6 mg, 86% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 37.4, 8.0 Hz, 2H), 7.15 (dt, *J* = 41.2, 7.4 Hz, 2H), 6.97–6.86 (m, 3H), 6.82–6.74 (m, 2H), 6.38 (d, *J* = 3.3 Hz, 1H), 5.88 (ddt, *J* = 16.7, 11.2, 5.8 Hz, 1H), 5.36–5.24 (m, 2H), 4.65–4.55 (m, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.08 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.05 – –114.17 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 247.1 Hz), 152.7, 136.2, 135.2, 132.1 (d, $J_{C–F}$ = 4.0 Hz), 130.8, 129.4, 129.3 (d, $J_{C–F}$ = 8.2 Hz), 128.8, 128.4, 122.7, 120.9, 120.8, 119.6, 115.3 (d, $J_{C–F}$ = 21.6 Hz), 111.2, 104.2, 69.5, 25.0, 12.6; IR (Neat Film, NaCl) 2974, 1766, 1681, 1604, 1510,

1456, 1333, 1238, 1208, 1144, 1119, 945, 835, 765, 743 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}FNO_3$ $[M+H]^+$: 366.1500, found 366.1502.



(*E*)-1-(1*H*-indol-1-yl)-2-(4-(trifluoromethyl)phenyl)but-1-en-1-yl allyl carbonate (1k)

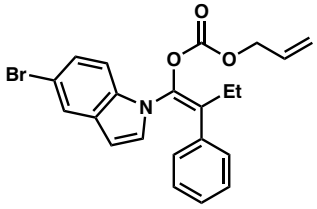
Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (375.1 mg, 90% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 1.0, 7.8 Hz, 1H), 7.49 (dq, *J* = 1.0, 8.2 Hz, 1H), 7.41–7.34 (m, 2H), 7.28–7.21 (m, 1H), 7.19–7.08 (m, 3H), 6.87 (d, *J* = 3.3 Hz, 1H), 6.40 (dd, *J* = 0.9, 3.4 Hz, 1H), 5.89 (ddt, *J* = 5.9, 10.5, 17.2 Hz, 1H), 5.38–5.25 (m, 2H), 4.63 (dt, *J* = 1.4, 5.8 Hz, 2H), 2.72 (q, *J* = 7.5 Hz, 2H), 1.11 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.73; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 140.2, 136.2, 136.0, 130.8, 129.5 (q, *J* = 32.5 Hz), 129.0, 128.8, 128.5, 128.1, 125.4 (q, *J* = 272 Hz), 125.4–125.2 (m), 123.0, 121.1, 121.0, 119.8, 111.2, 104.6, 69.7, 24.9, 12.6; IR (Neat Film, NaCl) 1766, 1681, 1617, 1456, 1325, 1260, 1239, 1211, 1167, 1123, 1067, 946, 834, 744 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{21}F_3NO_3$ $[M+H]^+$: 416.1468, found 416.1456.



(*E*)-allyl (1-(5-methyl-1*H*-indol-1-yl)-2-phenylbut-1-en-1-yl) carbonate (1l)

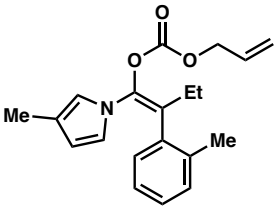
Purified by column chromatography (hexanes → 5% Et_2O in hexanes) to provide the desired product as a yellow oil (336.3 mg, 93% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.30–7.28 (m, 1H), 7.12–7.08 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.97 (dd, *J* = 6.4, 2.9 Hz, 2H), 6.83 (d, *J* = 3.3 Hz, 1H), 6.30–6.18 (m, 1H), 5.94–5.82 (m, 1H), 5.37–5.24 (m, 2H), 4.63–4.55 (m, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 136.3, 135.3, 134.6, 130.9, 130.0, 129.8, 129.1, 128.7, 128.3, 127.7, 127.5, 124.2, 120.6 119.5, 111.0, 103.6, 69.4, 25.0, 21.5, 12.7; IR (Neat Film, NaCl) 3023, 2974,

2875, 1766, 1682, 1470, 1377, 1330, 1260, 1230, 1209, 1163, 1125, 1095, 1042, 967, 946, 843, 796, 763, 718, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1751, found 362.1751.



(*E*)-allyl (1-(5-bromo-1*H*-indol-1-yl)-2-phenylbut-1-en-1-yl) carbonate (1m)

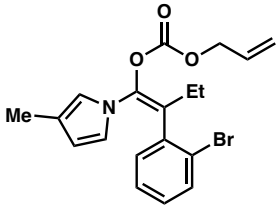
Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as an amorphous white solid (352.3 mg, 83% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.9 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.24 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.12–7.08 (m, 3H), 6.94 (dd, *J* = 6.7, 3.0 Hz, 2H), 6.91 (d, *J* = 3.4 Hz, 1H), 6.29 (d, *J* = 3.3 Hz, 1H), 5.92–5.82 (m, 1H), 5.36–5.24 (m, 2H), 4.61 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 136.0, 134.9, 134.5, 131.0, 130.8, 130.2, 130.1, 128.4, 127.8, 127.5, 125.5, 123.3, 119.8, 114.1, 112.8, 103.5, 69.6, 25.0, 12.6; IR (Neat Film, NaCl) 2973, 2934, 2873, 1764, 1679, 1452, 1375, 1236, 1208, 1128, 945, 758, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}BrNO_3$ $[M+H]^+$: 426.0699, found 426.0696.



(*E*)-allyl (1-(3-methyl-1*H*-pyrrol-1-yl)-2-(*o*-tolyl)but-1-en-1-yl) carbonate (1n)

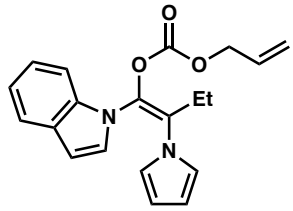
Purified by column chromatography (2.5% Et_2O in hexanes) to provide the desired product as a colorless oil (533.2 mg, 75% yield) Note: compound darkens in color overtime under argon at –20 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.17–7.07 (m, 4H), 6.34 (dd, *J* = 2.9, 2.2 Hz, 1H), 6.29 (ddd, *J* = 2.2, 1.7, 1.0 Hz, 1H), 5.95 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.76 (ddd, *J* = 2.9, 1.7, 0.5 Hz, 1H), 5.44–5.28 (m, 2H), 4.70 (dq, *J* = 5.8, 1.4 Hz, 2H), 2.44 (dq, *J* = 14.9, 7.3 Hz, 2H), 2.11 (d, *J* = 0.5 Hz, 3H), 1.91 (d, *J* = 1.0 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 136.5, 136.3, 136.3, 131.0, 130.2, 129.2, 127.5, 125.7, 122.8, 121.2, 119.6, 119.6, 118.2, 110.9, 69.5, 25.7, 19.4, 11.9, 11.8; IR (Neat Film, NaCl) 3061, 3019, 2972, 2936, 2874, 1769, 1688, 1487, 1456, 1350, 1258, 1234, 1185, 1139, 1118, 1070, 1047, 1022, 995, 958,

946, 915, 837, 761, 729, 694 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{24}NO_3$ $[M+H]^+$: 326.1751, found 326.1733.



(*E*)-allyl (2-(2-bromophenyl)-1-(3-methyl-1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1o)

Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a colorless oil (410 mg, 70% yield) Note: compound darkens in color overtime under argon at –20 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.18 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13–7.03 (m, 2H), 6.50 (dd, *J* = 2.8, 2.2 Hz, 1H), 6.40 (m, 1H), 5.95 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.77 (dd, *J* = 3.0, 1.7 Hz, 1H), 5.43–5.27 (m, 2H), 4.70 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.51 (ddq, *J* = 36.7, 14.5, 7.3 Hz, 2H), 1.92 (d, *J* = 1.0 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 137.7, 137.4, 132.9, 131.0, 130.9, 129.1, 127.3, 125.0, 123.7, 121.4, 119.8, 119.6, 118.6, 111.0, 69.6, 24.5, 11.9, 11.8; IR (Neat Film, NaCl) 2972, 2936, 1770, 1692, 1488, 1470, 1392, 1364, 1350, 1292, 1251, 1231, 1187, 1133, 1070, 1024, 959, 947, 758 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{21}BrNO_3$ $[M+H]^+$: 390.0699, found 390.0688.



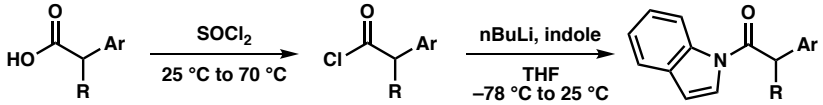
(*E*)-1-(1*H*-indol-1-yl)-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl allyl carbonate (1p)

Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a viscous colorless oil (2.33 g, 88% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.42 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.21 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.14 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.89 (d, *J* = 3.4 Hz, 1H), 6.48 (dd, *J* = 3.4, 0.9 Hz, 1H), 6.38–6.32 (m, 2H), 6.02–5.97 (m, 2H), 5.87 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.38–5.24 (m, 2H), 4.61 (dt, *J* = 5.9, 1.3 Hz, 2H), 2.72 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.1, 132.6, 130.7, 130.1, 128.7, 127.8, 123.1, 121.2, 121.0, 120.2, 120.0, 110.8, 109.8, 69.9,

24.2, 11.7; IR (Neat Film, NaCl) 2979, 2879, 1769, 1703, 1520, 1482, 1456, 1383, 1482, 1456, 1347, 1247, 1212, 1163, 1117, 1086, 968, 944, 894, 827, 765, 743, 724 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547, found 337.1555.

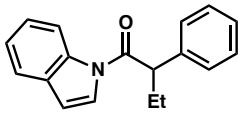
Preparation of *N*-Acyl Indoles

General Procedure 1



To an oven-dried vial containing α-aryl carboxylic acid (1.2 equiv) was added $SOCl_2$ neat (2.4 equiv) and the resulting mixture stirred at 25 °C for 20 min then 70 °C for 2 h (note: effluent gas flow is bubbled through a glass tube packed with powdered NaOH). The reaction was then concentrated in vacuo to afford the crude acid chloride, which was used in the next step without further purification.

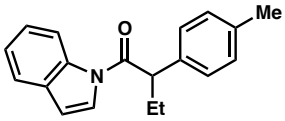
A flame-dried flask containing indole (1.0 equiv) in THF (500 mM) was cooled to 0 °C in an ice bath and n-BuLi (1.05 equiv) was added dropwise. The mixture was stirred at 0 °C for 15 min then cooled to –78 °C in a dry-ice acetone bath. The crude acid chloride dissolved in THF is then added quickly, and the resulting mixture allowed to slowly warm to room temperature. Then reaction was then quenched with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and the desired *N*-acyl indole isolated by silica gel flash chromatography.



1-(1*H*-indol-1-yl)-2-phenylbutan-1-one (SI1)

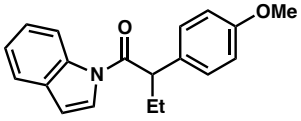
Prepared according to general procedure 1. Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a white solid (428.2 mg, 81% yield); ^1H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.3, 1H), 7.51–7.42 (m, 2H), 7.38–7.13 (m, 7H), 6.48 (d, *J* = 3.8 Hz, 1H), 4.10 (t, *J* = 7.2 Hz, 1H), 2.35–2.18 (m, 1H), 1.89 (dt, *J* = 13.7, 7.2 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.9, 139.1, 136.0, 130.3, 129.1, 127.7, 127.5,

125.2, 124.9, 123.8, 120.8, 117.0, 109.1, 53.7, 27.9, 12.3; IR (Neat Film, NaCl) 3063, 2967, 2943, 2874, 1704, 1602, 1584, 1539, 1472, 1451, 1384, 1355, 1328, 1304, 1222, 1208, 1181, 1154, 1082, 1017, 903, 880, 825, 807, 766, 749, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383, found 264.1377.



1-(1*H*-indol-1-yl)-2-(*p*-tolyl)butan-1-one (SI2)

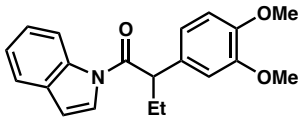
Prepared according to general procedure 1. Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a yellow oil (901.0 mg, 76% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.53–7.46 (m, 2H), 7.35 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.27–7.22 (m, 3H), 7.16–7.09 (m, 2H), 6.52 (dd, *J* = 3.8, 0.8 Hz, 1H), 4.11 (t, *J* = 7.2 Hz, 1H), 2.36–2.21 (m, 4H), 1.91 (dp, *J* = 13.7, 7.4 Hz, 1H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 137.0, 136.1, 136.0, 130.3, 129.8, 127.5, 125.0, 124.9, 123.7, 120.7, 116.9, 108.9, 53.3, 27.8, 21.0, 12.2; IR (Neat Film, NaCl) 3051, 3024, 2966, 2931, 2874, 1704, 1584, 1539, 1514, 1472, 1451, 1384, 1355, 1325, 1304, 1223, 1208, 1187, 1155, 1084, 904, 808, 785, 767, 751, 715 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1531.



1-(1*H*-indol-1-yl)-2-(4-methoxyphenyl)butan-1-one (SI3)

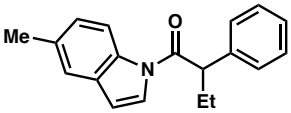
Prepared according to general procedure 1. Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a yellow oil containing minor impurities (1.2439 g, 85% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.53–7.48 (m, 2H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.30–7.22 (m, 3H), 6.89–6.82 (m, 2H), 6.53 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.10 (t, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 2.37–2.20 (m, 1H), 1.90 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 158.9, 135.9, 131.1, 130.3, 128.7, 125.1, 124.9, 123.7, 120.7, 116.9, 114.4, 108.9, 55.1, 52.8, 27.8, 12.2; IR (Neat Film, NaCl) 2964, 2933, 1702, 1610, 1540, 1511, 1450, 1384, 1354, 1324, 1302, 1252, 1222, 1207, 1179, 1154, 1033, 904, 820,

788, 766, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}NO_2$ $[M+H]^+$: 294.1489, found 294.1494.



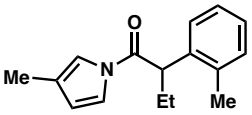
2-(3,4-dimethoxyphenyl)-1-(1*H*-indol-1-yl)butan-1-one (SI4)

Prepared according to general procedure 1. Purified by column chromatography (20 → 30% Et_2O in hexanes) to provide the desired product as a yellow oil (838.3 mg, 62% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.54–7.49 (m, 2H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.29–7.22 (m, 1H), 6.92–6.85 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.54 (dd, *J* = 3.8, 0.8 Hz, 1H), 4.08 (t, *J* = 7.3 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.28 (dt, *J* = 13.7, 7.3 Hz, 1H), 1.92 (dt, *J* = 13.8, 7.3 Hz, 1H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 149.5, 148.4, 136.0, 131.6, 130.3, 125.2, 124.9, 123.8, 120.8, 120.2, 116.9, 111.5, 110.3, 109.1, 56.0, 55.9, 53.4, 27.9, 12.3; IR (Neat Film, NaCl) 2964, 2934, 1699, 1591, 1516, 1451, 1355, 1326, 1302, 1262, 1242, 1206, 1152, 1027, 790, 766, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}NO_3$ $[M+H]^+$: 324.1594, found 324.1588.



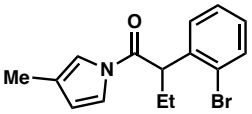
1-(5-methyl-1*H*-indol-1-yl)-2-phenylbutan-1-one (SI5)

Prepared according to general procedure 1. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a cream-colored solid (567.3 mg, 82% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 3.7 Hz, 1H), 7.38–7.27 (m, 5H), 7.28–7.20 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 3.7 Hz, 1H), 4.14 (t, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.31 (dtd, *J* = 14.7, 7.3, 1.0 Hz, 1H), 1.99–1.89 (m, 1H), 0.99 (td, *J* = 7.4, 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 139.3, 134.2, 133.4, 130.6, 129.2, 127.8, 127.5, 126.5, 124.9, 120.7, 116.6, 109.0, 53.7, 27.9, 21.5, 12.4; IR (Neat Film, NaCl) 3027, 2967, 2931, 2874, 1703, 1582, 1541, 1468, 1382, 1328, 1304, 1208, 1182, 1089, 903, 833, 823, 811, 740, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1534.



1-(3-methyl-1*H*-pyrrol-1-yl)-2-(*o*-tolyl)butan-1-one (SI6)

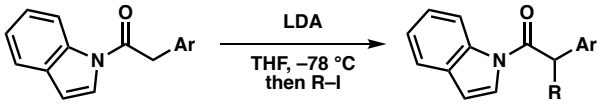
Prepared according to general procedure 1. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a light yellow oil (539.3 mg, 54% yield) Note: compound darkens in color overtime under argon at –20 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–6.92 (m, 6H), 6.03 (dd, *J* = 3.3, 1.6 Hz, 1H), 4.24 (dd, *J* = 8.5, 5.7 Hz, 1H), 2.47 (s, 3H), 2.20 (ddq, *J* = 14.5, 8.5, 7.3 Hz, 1H), 2.00 (d, *J* = 1.2 Hz, 3H), 1.84–1.64 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 137.9, 134.6, 131.0, 127.3, 127.0, 126.8, 123.8, 119.3, 116.5, 115.4, 48.5, 27.4, 19.8, 12.7, 12.1; IR (Neat Film, NaCl) 3021, 2964, 2928, 2874, 1708, 1488, 1459, 1396, 1355, 1327, 1306, 1192, 1171, 1082, 1066, 952, 905, 834, 820, 780, 756, 730 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{16}H_{20}NO$ $[M+H]^+$: 242.1539, found 242.1532.



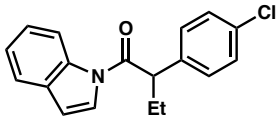
2-(2-bromophenyl)-1-(3-methyl-1*H*-pyrrol-1-yl)butan-1-one (SI7)

Prepared according to general procedure 1. Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a yellow oil (1.56 g, 72% yield) Note: compound darkens in color overtime under argon at –20 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.28–7.22 (m, 2H), 7.11 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 2H), 6.07 (dd, *J* = 3.3, 1.6 Hz, 1H), 4.62 (dd, *J* = 8.2, 6.1 Hz, 1H), 2.16 (ddq, *J* = 13.7, 8.2, 7.3 Hz, 1H), 2.03 (d, *J* = 1.2 Hz, 3H), 1.83 (dqd, *J* = 13.6, 7.4, 6.2 Hz, 1H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 138.7, 133.2, 129.0, 128.4, 128.4, 124.1, 124.1, 119.5, 116.6, 115.7, 50.7, 27.6, 12.3, 12.1; IR (Neat Film, NaCl) 2967, 2930, 2875, 1709, 1489, 1471, 1440, 1398, 1356, 1328, 1306, 1200, 1180, 1067, 1020, 908, 830, 810, 749 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{17}BrNO$ $[M+H]^+$: 306.0488, found 306.0477.

General Procedure 2

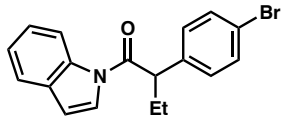


A flame-dried round bottom flask was charged with *i*-Pr_2NH (367 μL, 2.60 mmol, 1.3 equiv) and THF (18.0 mL). The solution was then cooled in a 0 ºC ice bath for 10 min and a 2.40 M solution of *n*-BuLi (996 μL, 2.40 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, the solution was cooled in a –78 ºC acetone/dry ice bath for 15 min, after which time a solution of acyl indole (498.6 mg, 2.00 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise over 5 min. After stirring at –78 ºC for 1 h, neat ethyl iodide (193 μL, 2.40 mmol, 1.2 equiv) was then added dropwise. The reaction mixture was allowed to slowly warm to 20 ºC, and then heated to 65 ºC and stirred for 16 h, after which time the reaction was quenched with the slow addition of 10 mL H_2O. The mixture was then transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted 3 x 10 mL Et_2O and the combined organics were dried over Na_2SO_4, filtered, and concentrated. The desired *N*-acyl indole was isolated by silica gel flash chromatography.



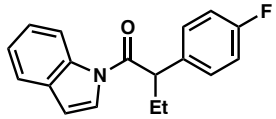
2-(4-chlorophenyl)-1-(1*H*-indol-1-yl)butan-1-one (SI8)

Prepared according to General Procedure 2 with (539.5 mg, 2.00 mmol, 1.0 equiv) of acyl indole. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a light yellow oil (373.8 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.52 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.44 (d, *J* = 3.8 Hz, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.30 (s, 4H), 7.28–7.24 (m, 1H), 6.56 (dd, *J* = 3.9, 0.8 Hz, 1H), 4.13 (t, *J* = 7.3 Hz, 1H), 2.29 (dt, *J* = 13.8, 7.3 Hz, 1H), 2.03–1.76 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.6, 136.0, 133.5, 130.4, 129.4, 129.2, 125.4, 124.6, 124.0, 120.9, 117.0, 109.5, 53.1, 27.9, 12.3; IR (Neat Film, NaCl) 2967, 2361, 1700, 1540, 1491, 1451, 1384, 1354, 1328, 1302, 1221, 1207, 1094, 1015, 904, 814, 794, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}ClNO$ $[M+H]^+$: 298.0993, found 298.0984.



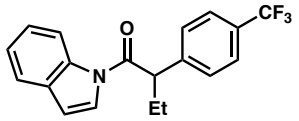
2-(4-bromophenyl)-1-(1*H*-indol-1-yl)butan-1-one (SI9)

Prepared according to General Procedure 2 with (628.4 mg, 2.00 mmol, 1.0 equiv) of acyl indole. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (451.0 mg, 66% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.48–7.41 (m, 3H), 7.38–7.32 (m, 1H), 7.30–7.20 (m, 3H), 6.56 (d, *J* = 3.8 Hz, 1H), 4.12 (t, *J* = 7.2 Hz, 1H), 2.29 (dp, *J* = 14.6, 7.3 Hz, 1H), 1.92 (dp, *J* = 14.6, 7.3 Hz, 1H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 138.1, 136.0, 132.3, 130.4, 129.6, 125.4, 124.6, 124.0, 121.6, 120.9, 117.0, 109.5, 53.2, 27.9, 12.3; IR (Neat Film, NaCl) 3052, 2967, 2931, 2874, 1703, 1486, 1451, 1383, 1354, 1327, 1301, 1207, 1154, 1074, 1011, 904, 880, 812, 792, 755, 751, 713 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}BrNO$ $[M+H]^+$: 342.0488, found 342.0497.



2-(4-fluorophenyl)-1-(1*H*-indol-1-yl)butan-1-one (SI10)

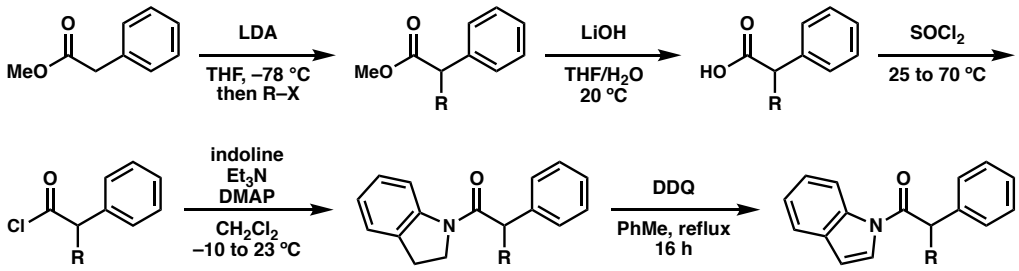
Prepared according to General Procedure 2 with (506.6 mg, 2.00 mmol, 1.0 equiv) of acyl indole. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (360.4 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.3 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.46 (d, *J* = 3.8 Hz, 1H), 7.39–7.29 (m, 3H), 7.30–7.22 (m, 1H), 7.07–6.97 (m, 2H), 6.56 (dd, *J* = 3.8, 0.6 Hz, 1H), 4.15 (t, *J* = 7.3 Hz, 1H), 2.30 (dt, *J* = 13.8, 7.3 Hz, 1H), 1.92 (dq, *J* = 14.1, 7.3 Hz, 1H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.9 (tt, *J* = 8.5, 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 162.1 (d, $J_{C–F}$ = 246.2 Hz), 136.0, 134.8 (d, $J_{C–F}$ = 3.3 Hz), 130.3, 129.4 (d, $J_{C–F}$ = 8.0 Hz), 125.3, 124.7, 123.9, 120.9, 117.0, 116.0 (d, $J_{C–F}$ = 21.5 Hz), 109.3, 52.8, 27.9, 12.2; IR (Neat Film, NaCl) 3074, 2967, 2934, 2873, 1702, 1603, 1508, 1450, 1384, 1354, 1327, 1301, 1222, 1207, 1158, 818, 792, 752, 714 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}FNO$ $[M+H]^+$: 282.1289, found 282.1286.



1-(1*H*-indol-1-yl)-2-(4-(trifluoromethyl)phenyl)butan-1-one (SI11)

Prepared according to General Procedure 2. Purified by column chromatography (6% Et_2O in hexanes) to provide the desired product as a white solid (190.8 mg, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.62–7.58 (m, 2H), 7.55–7.48 (m, 3H), 7.44 (d, *J* = 3.9 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.30–7.25 (m, 1H), 6.57 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.23 (t, *J* = 7.3 Hz, 1H), 2.41–2.26 (m, 1H), 1.95 (dt, *J* = 13.8, 7.3 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.6; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 143.0 (d, *J* = 1.5 Hz), 136.0, 130.4, 129.9 (q, *J* = 32.6 Hz), 128.3, 126.1 (q, *J* = 3.8 Hz), 125.5, 125.4 (q, *J* = 272.4 Hz), 124.5, 124.1, 121.0, 117.0, 109.7, 53.5, 28.0, 12.3; IR (Neat Film, NaCl) 1702, 1451, 1384, 1354, 1324, 1304, 1208, 1166, 1123, 1068, 1068, 1018, 831, 800, 766, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{17}F_3NO$ $[M+H]^+$: 332.1257, found 332.1248.

General Procedure 3



A flame-dried round bottom flask was charged with *i*-Pr_2NH (1.82 mL, 13.0 mmol, 1.3 equiv) and THF (15 mL). The solution was then cooled in a 0 ºC ice bath for 10 min and a 2.40 M solution of *n*-BuLi (5.0 mL, 12.0 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, the solution was cooled in a –78 ºC acetone/dry ice bath for 15 min, after which time a solution of methyl phenyl acetate (1.41 mL, 10.0 mmol, 1.0 equiv) in THF (29 mL) was added dropwise over 10 min. After stirring at –78 ºC for 1 h, the appropriate electrophile (1.5 equiv) was then added neat dropwise. The reaction mixture was allowed to slowly warm to 20 ºC and stirred for 16 h after which time the reaction was quenched with the slow addition of 30 mL of

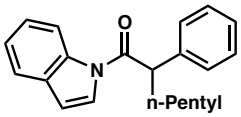
sat. aq. NH_4Cl. The mixture was then transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted 3 x 20 mL EtOAc and the combined organics were dried over Na_2SO_4, filtered, and concentrated.

The crude material was then transferred to a round bottom flask and dissolved in THF (28 mL) and H_2O (20 mL). To the solution was then added LiOH (479.0 mg, 20.0 mmol, 2.0 equiv) and the resulting reaction mixture was stirred at 20 ºC for 16 h. The mixture was then transferred to a separatory funnel and washed with 2 x 5 mL Et_2O. The aqueous layer was then slowly acidified to pH 1 with 2.0 N HCl and extracted 2 x 10 mL Et_2O. The combined organics were dried over Na_2SO_4, filtered, and concentrated. The crude acid was used in the next step without further purification.

To an oven-dried flask containing α-aryl carboxylic acid (5.0 mmol, 1.0 equiv) was added $SOCl_2$ neat (620 μL, 1.7 equiv) and the resulting mixture stirred at 25 °C for 20 min then 70 °C for 2 h (note: effluent gas flow is bubbled through a glass tube packed with powdered NaOH). The reaction was then concentrated in vacuo to afford the crude acid chloride, which was used in the next step without further purification.

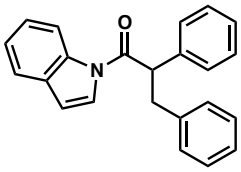
A separate flame-dried flask containing freshly distilled indoline (4.20 mmol, 1.0 equiv), Et_3N (1.17 mL, 8.40 mmol, 2.0 equiv), and DMAP (25.7 mg, 0.21 mmol, 0.05 equiv) in CH_2Cl_2 (42 mL) was cooled to –10 °C in an acetone/ice bath and the crude acid chloride (5.0 mmol, 1.2 equiv) dissolved in CH_2Cl_2 (21 mL) was added dropwise via cannula transfer. The mixture was stirred at –10 °C for 15 min then warmed to 23 ºC and stirred for 18 h. The reaction mixture was quenched with saturated $NaHCO_3$ (20 mL) and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted twice with CH_2Cl_2 (20 mL). The combined organics were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford the crude amide which was used in the next step without further purification.

The crude amide prepared above was transferred to a round bottom flask affixed with a reflux condenser. Dry toluene (42 mL) and DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) (1.14 g, 5.0 mmol, 1.2 equiv) were then added and the resulting dark red reaction solution was heated to reflux for 16 h. The crude reaction mixture was then filtered through a pad of celite with toluene, concentrated, and purified via flash column chromatography to afford the desired acyl indole.



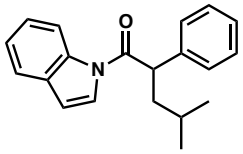
1-(1*H*-indol-1-yl)-2-phenylheptan-1-one (SI12)

Prepared according to General Procedure 3 with *n*-pentyl iodide (1.96 mL, 15.0 mmol, 1.5 equiv). Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a colorless oil (319.5 mg, 25% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.54–7.48 (m, 2H), 7.39–7.30 (m, 5H), 7.30–7.21 (m, 2H), 6.54 (dd, *J* = 3.8, 0.8 Hz, 1H), 4.25 (t, *J* = 7.2 Hz, 1H), 2.34–2.25 (m, 1H), 1.90 (tdd, *J* = 12.9, 8.5, 5.7 Hz, 1H), 1.46–1.25 (m, 6H), 0.91–0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 139.4, 136.0, 130.3, 129.2, 127.7, 127.5, 125.2, 124.8, 123.8, 120.7, 117.0, 109.1, 52.1, 34.7, 31.8, 27.4, 22.6, 14.1; IR (Neat Film, NaCl) 3063, 3029, 2954, 2928, 2858, 1704, 1602, 1584, 1539, 1451, 1384, 1353, 1311, 1207, 1154, 1102, 941, 919, 880, 766, 749, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1846, found 306.1846.



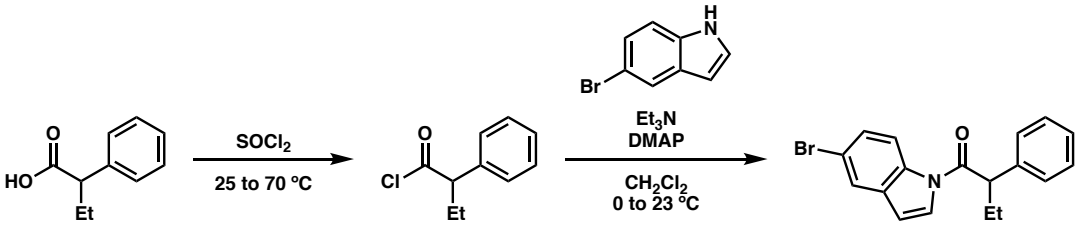
1-(1*H*-indol-1-yl)-2,3-diphenylpropan-1-one (SI13)

Prepared according to General Procedure 3 with BnBr (1.78 mL, 15.0 mmol, 1.5 equiv). Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (830.7 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.48 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.39 (d, *J* = 3.8 Hz, 1H), 7.34 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.26 – 7.10 (m, 7H), 6.48 (dd, *J* = 3.9, 0.7 Hz, 1H), 4.51 (t, *J* = 7.2 Hz, 1H), 3.67 (dd, *J* = 13.7, 7.6 Hz, 1H), 3.14 (dd, *J* = 13.8, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.7, 136.0, 130.3, 129.3, 129.2, 128.5, 127.8, 127.7, 126.6, 125.3, 124.8, 123.9, 120.8, 117.0, 109.3, 54.4, 40.8; IR (Neat Film, NaCl) 3155, 3062, 3029, 2927, 1950, 1805, 1698, 1601, 1585, 1539, 1495, 1472, 1453, 1385, 1354, 1319, 1300, 1221, 1207, 1108, 1074, 911, 898, 766, 749, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{20}NO$ $[M+H]^+$: 326.1539, found 326.1536.



1-(1*H*-indol-1-yl)-4-methyl-2-phenylpentan-1-one (SI14)

Prepared according to General Procedure 3 with *i*-butyl iodide (1.73 mL, 15.0 mmol, 1.5 equiv). Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (1.2177 g, 99% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 3.8 Hz, 1H), 7.52–7.50 (m, 1H), 7.39–7.29 (m, 5H), 7.27–7.22 (m, 2H), 6.55 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.37 (t, *J* = 7.3 Hz, 1H), 2.22 (dt, *J* = 13.6 Hz, 7.4 Hz, 1H), 1.79 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.61 (dp, *J* = 13.5, 6.8 Hz, 1H), 0.97 (dd, *J* = 27.5, 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 139.5, 136.1, 130.4, 129.3, 127.8, 127.5, 125.3, 124.8, 123.9, 120.9, 117.1, 109.3, 49.8, 43.8, 25.9, 22.9, 22.7; IR (Neat Film, NaCl) 3386, 3154, 3063, 3029, 2956, 2868, 1703, 1602, 1585 1538, 1493, 1471, 1451, 1385, 1344, 1332, 1308, 1295, 1222, 1207, 1103, 1084, 1018, 943, 886, 766, 748, 670 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1696, found 292.1696.



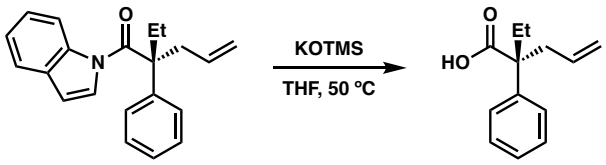
1-(5-bromo-1*H*-indol-1-yl)-2-phenylbutan-1-one (SI15)

To a flame-dried conical flask containing α-aryl carboxylic acid (1 equiv) was added $SOCl_2$ neat (2 equiv) and the resulting mixture stirred at 25 °C for 20 min then 70 °C for 2 h (note: effluent gas flow is bubbled through a glass tube packed with powdered NaOH). The reaction was then concentrated in vacuo to afford the crude acid chloride, which was used in the next step without further purification.

To a flame-dried 25 mL round bottom flask was added 5-bromoindole (588.1 mg, 3.00 mmol, 1.0 equiv), DMAP (36.7 mg, 0.30 mmol, 0.10 equiv), CH_2Cl_2 (5.0 mL), and Et_3N (627 μL, 4.50 mmol, 1.5 equiv). The resulting clear, colorless solution was then cooled in a 0 ºC ice bath for 10 min before a solution of the above crude acid chloride in CH_2Cl_2 (3.0 mL) was added dropwise via cannula. The resulting bright yellow solution was stirred at 23 ºC for 18 h then concentrated under reduced pressure. The crude yellow oil was then dissolved in Et_2O (10 mL), transferred to

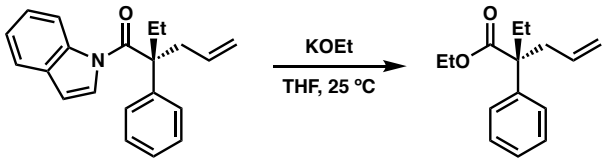
a separatory funnel, and washed with H_2O (20 mL). The aqueous layer was then extracted with Et_2O (3 x 10 mL). The combined organics were then washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford an orange oil which was purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as an off white solid with minor impurities (654.3 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 3.8 Hz, 1H), 7.44 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38–7.30 (m, 4H), 7.30–7.22 (m, 1H), 6.46 (d, *J* = 3.8 Hz, 1H), 4.12 (t, *J* = 7.2 Hz, 1H), 2.30 (dt, *J* = 14.1, 7.3 Hz, 1H), 1.95 (dt, *J* = 14.1, 7.01 Hz, 1H), 0.98 (t, *J* = 7.3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 138.8, 134.6, 132.0, 129.2, 127.9, 127.7, 127.6, 125.9, 123.4, 118.3, 117.0, 108.2, 53.7, 27.8, 12.3; IR (Neat Film, NaCl) 3063, 3028, 2967, 2932, 2874, 1704, 1575, 1534, 1444, 1377, 1325, 1304, 1217, 1199, 1181, 1088, 896, 826, 810, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}BrNO$ $[M+H]^+$: 342.0488, found 342.0478.

Derivatization of Alkylation Products



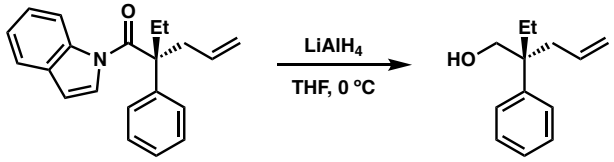
(*R*)-2-ethyl-2-phenylpent-4-enoic acid (3)

To a flame-dried round bottom flask containing a stirred suspension of KOTMS (162 mg, 1.26 mmol) in THF (1.5 mL) was added a solution of acyl indole ***2a*** (38.2 mg, 0.126 mmol) in THF (1.5 mL). The resulting mixture was placed in a 60 °C oil bath and stirred for 16 h. The crude reaction was diluted with Et_2O and 5 M NaOH, and the layers separated. The aqueous layer was washed with Et_2O and acidified with 4 M HCl to pH 1. The aqueous layer was extracted with Et_2O three times and the combined organic layers washed with water, dried over $MgSO_4$, and concentrated to a light yellow solid (25.6 mg, 99% yield), $[\alpha]_D^{25}$ –30.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.17 (m, 5H), 5.54 (dddd, *J* = 17.0, 10.1, 7.6, 6.8 Hz, 1H), 5.16–4.96 (m, 2H), 2.81 (qdt, *J* = 14.1, 6.8, 1.2 Hz, 2H), 2.22–1.90 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 141.5, 133.5, 128.5, 127.1, 126.8, 118.5, 54.0, 38.4, 26.9, 8.5; IR (Neat Film, NaCl) 3064, 2975, 1699, 1498, 1447, 1401, 1252, 918, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1223, found 205.1213.



ethyl (*R*)-2-ethyl-2-phenylpent-4-enoate (4)

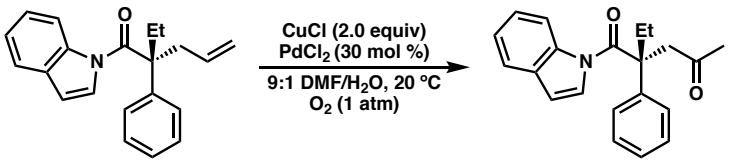
To a flame-dried round bottom flask containing a stirred solution of KOEt (32.2 mg, 0.383 mmol) in THF (1.5 mL) was added a solution of acyl indole ***2a*** (38.7 mg, 0.128 mmol) and the resulting mixture stirred at 25 °C for 15 h. The crude reaction was diluted with Et_2O and quenched with saturated NH_4Cl, and the layers separated. The aqueous layer was extracted with Et_2O and the combined organic fractions dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel flash chromatography (5% Et_2O in hexanes) to provide the desired product as a colorless oil (22.3 mg, 75% yield), $[\alpha]_D^{25}$ –4.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.07 (m, 5H), 5.46 (dddd, *J* = 16.9, 10.1, 7.8, 6.7 Hz, 1H), 5.07–4.87 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.87–2.58 (m, 2H), 2.13–1.87 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 142.4, 133.8, 128.3, 126.7, 126.6, 118.2, 60.8, 54.1, 38.7, 27.1, 14.2, 8.5; IR (Neat Film, NaCl) 2976, 2360, 1728, 1220, 1135, 1030, 916, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1536, found 233.1531.



(*R*)-2-ethyl-2-phenylpent-4-en-1-ol (5)

To a flame-dried round bottom flask was added acyl indole ***2a*** (32.6 mg, 0.107 mmol, 1.0 equiv) and THF (2.1 mL). The resulting solution was cooled to 0 ºC for 5 min and then a 1.0 M solution of $LiAlH_4$ (320 mL, 0.320 mmol, 3.0 equiv) was added dropwise. The resulting solution was stirred at 0 ºC for 5 min, then diluted with Et_2O (2.1 mL) and quenched with the addition of H_2O (12 μL) followed by 15% w/v $NaOH/H_2O$ (12 μL), and an additional portion of H_2O (36 μL). The resulting gray suspension was warmed to 20 ºC and stirred vigorously for 15 min. $MgSO_4$ (50 mg) was added and the resulting suspension was stirred for 15 min and filtered through a plug of celite with Et_2O. The crude product was purified by silica gel flash chromatography

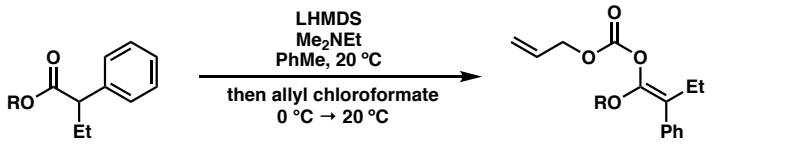
(10% Et_2O in hexanes) to provide the desired product as a colorless oil (17.2 mg, 84% yield); $[\alpha]_D^{25}$ +12.9 (*c* 0.65, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.31 (m, 4H), 7.23 (td, *J* = 6.4, 2.3 Hz, 1H), 5.70 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.18–5.01 (m, 2H), 3.82–3.70 (m, 2H), 2.55 (ddd, *J* = 61.6, 13.9, 7.2 Hz, 2H), 1.73 (q, *J* = 7.4 Hz, 2H), 1.34 (s, 1H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 134.9, 128.6, 127.0, 126.3, 117.8, 67.9, 46.3, 38.6, 27.5, 8.0; IR (Neat Film, NaCl) 3399 (br), 3060, 3024, 3004, 2966, 2934, 2880, 2361, 1638, 1497, 1459, 1456, 1379, 1045, 1001, 914, 760, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{22}NO$ $[M+NH_4]^+$: 208.1696, found 208.1692.



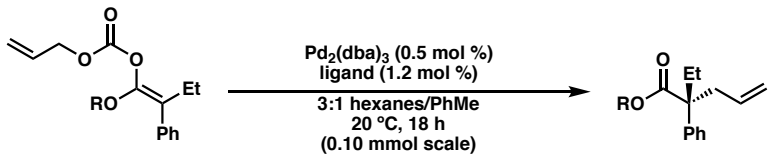
(*R*)-2-ethyl-1-(1*H*-indol-1-yl)-2-phenylpentane-1,4-dione (6)

To a round bottom flask containing acyl indole ***2a*** (33.1 mg, 0.109 mmol, 1.0 equiv) dissolved in 2.5 mL of 9:1 DMF/H_2O was added $PdCl_2$ (5.8 mg, 0.033 mmol, 0.30 equiv) and CuCl (21.6 mg, 0.218 mmol, 2.0 equiv). The flask was then quickly evacuated and backfilled three times with a balloon of O_2, and then stirred at 20 ºC under a balloon of O_2 for 48 h. The crude reaction was then diluted with EtOAc (2 mL) followed by brine (2 mL). The layers were separated and the aqueous layer was extracted with EtOAc (5 mL) twice. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel flash chromatography (10% Et_2O in hexanes) to afford the desired product as a white foam in a 5:1 ketone/aldehyde ratio (33.2 mg, 0.104 mmol, 95% yield); $[\alpha]_D^{25}$ –198.3 (*c* 1.45, $CHCl_3$); $[\alpha]_D^{25}$ –194.5 (*c* 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.31–7.23 (m , 5H), 7.23–7.12 (m, 2H), 6.70 (d, *J* = 3.9 Hz, 1H), 6.18 (d, *J* = 3.8 Hz, 1H), 3.26 (d, *J* = 15.4 Hz, 1H), 3.14 (d, *J* = 15.5 Hz, 1H), 2.64 (dq, *J* = 14.9, 7.5 Hz, 1H), 2.32–2.15 (m, 1H), 1.68 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 173.5, 142.1, 136.5, 129.3, 127.7, 126.5, 125.7, 125.2, 123.8, 120.5, 117.1, 108.4, 108.4, 55.8, 48.5, 32.1, 27.5, 8.9; IR (Neat Film, NaCl) 3163, 3056, 3056, 2972, 1721, 1697, 1537, 1450, 1308, 1206, 1076, 882, 768, 752, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1645, found 320.1630.

Challenging Substrate Classes



R = Ph, >98:2 E:Z, 32% yield
R = Et, >98:2 E:Z, 56% yield
R = *t*-Bu, >98:2 E:Z, 60% yield



entry	R	ligand	E:Z ratio	*yield*	*% ee*
1	Ph	*L1*	>98:2	trace	ND
2	Ph	*L2*	>98:2	trace	ND
3	Et	*L1*	>98:2	43	0
4	Et	*L2*	>98:2	trace	ND
5	*t*-Bu	*L1*	>98:2	trace	ND
6	*t*-Bu	*L2*	>98:2	trace	ND

Conditions: 0.10 mmol substrate, 0.5 mol % $Pd_2(dba)_3$, 1.2 mol % ligand 1.0 mL solvent.

Figure S1. Selective enolization of esters and attempted palladium-catalyzed allylic alkylation.

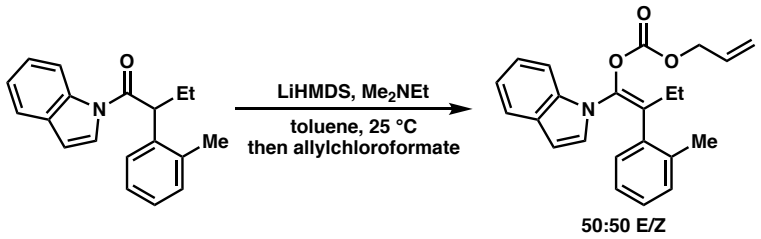
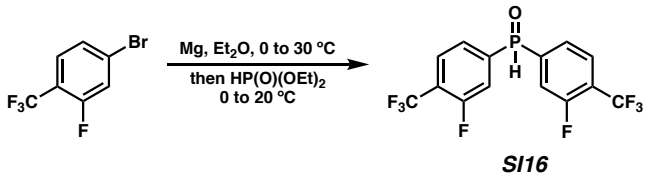


Figure S2. Poor enolization selectivity observed for *ortho*-substituted α–aryl substrates.

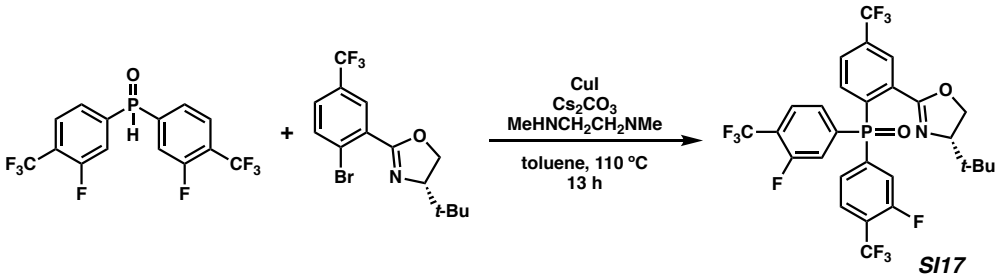
Ligand Synthesis



Bis(3-fluoro-4-(trifluoromethyl)phenyl)phosphine oxide (SI16)

According to the procedure of Stoltz[2]; A flame-dried 50 mL round bottomed flask was charged with magnesium turnings (804.7 mg, 33.1 mmol, 3.1 equiv) and Et_2O (17.8 mL). The mixture was cooled to 0 ºC and 4-bromo-2-fluoro-1-(trifluoromethyl)benzene (4.52 mL, 32.0 mmol, 3.0

equiv) was added dropwise over 15 min during which the reaction mixture turned from colorless to brown to black. A reflux condenser was then attached to the flask, and the mixture was warmed to 30 ºC in a water bath and stirred for 1 h. The resulting black solution was then canula transferred to a second 50 mL flame-dried round bottom flask to remove residual magnesium turnings. The resulting solution was then cooled to 0 ºC and neat diethyl phosphite (1.38 mL, 10.7 mmol, 1.0 equiv) was added dropwise over 10 min. The black reaction mixture was then allowed to warm to 20 ºC over 1 h and stirred for 24 h. The reaction mixture was then cooled to 0 ºC and 2.0 N HCl (20 mL) was added dropwise with vigorous stirring, leading to the precipitation of a brown solid. The mixture was then allowed to warm to 20 ºC and extracted with EtOAc (3 x 10 mL). The combined organic layers were then washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to an orange oil. Purification by silica gel chromatography (30% EtOAc in hexanes → 60% EtOAc in hexanes) provided the desired product as a yellow solid (2.6803 g, 7.72 mmol, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.80 (td, *J* = 7.2, 3.2 Hz, 2H), 7.59 (ddd, *J* = 19.8, 13.7, 8.6 Hz, 4H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.02 (d, *J* = 12.7 Hz), –110.40 – –110.63 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.77; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (dd, J = 262.9, 17.6 Hz), 137.2 (dd, J = 98.7, 6.0 Hz), 128.7 (dq, J = 14.0, 4.4 Hz), 126.3 (dd, J = 11.1, 4.4 Hz), 123.7–122.4 (m), 121.8 (q, J = 273.2 Hz), 119.2 (dd, J = 22.0, 12.5 Hz); IR (Neat Film, NaCl) 3040, 2368, 1622, 1576, 1498, 1409, 1323, 1239, 1178, 1134, 1043, 951, 901, 833, 696, 632 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{14}H_8F_8OP$ $[M+H]^+$: 375.0180, found 375.0172.

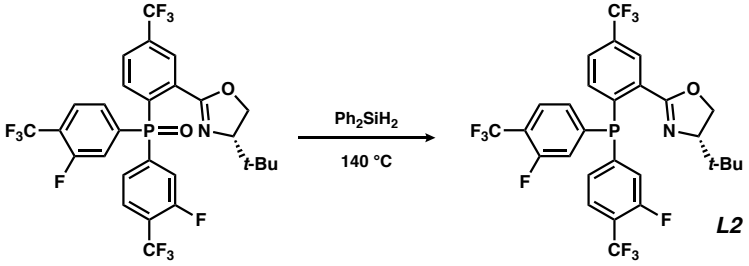


SI17

(*S*)-(2-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)-4-(trifluoromethyl)phenyl)bis(3-fluoro-4-(trifluoromethyl)phenyl)phosphine oxide (SI17)

To a flame-dried 100 mL two-necked round bottom flask equipped with a reflux condenser and glass stopper was added phosphine oxide **SI16** (2.4321 g, 6.50 mmol, 1.3 equiv), CuI (952.3 mg, 5.00 mmol, 1.0 equiv), and toluene (11.4 mL) followed by *N*,*N*'-dimethylethylenediamine (1.61 mL, 15.0 mmol, 3.0 equiv). The resulting green solution was stirred at 20 ºC for 20 min after

which time oxazoline (1.75 g, 5.00 mmol, 1.0 equiv), Cs_2CO_3 (6.03 g, 18.5 mmol, 3.7 equiv), and toluene (4.9 mL) were added. The flask was then immersed in a 110 ºC oil bath and the reaction suspension gradually turned blue and then orange. After 13 h, the reaction was cooled to 20 ºC and the orange reaction mixture was loaded directly onto a silica gel column (hexanes → 25% EtOAc in hexanes) to provide a white foam (841.9 mg, 26% yield); $[\alpha]_D^{25}$ –47.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 3.9, 1.8 Hz, 1H), 8.13–8.01 (m, 1H), 7.91–7.87 (m, 1H), 7.80–7.60 (m, 4H), 7.50–7.39 (m, 2H), 4.03 – 3.93 (m, 2H), 3.42 (dd, *J* = 10.2, 9.4 Hz, 1H), 0.72 (s, 9H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 26.10; ^{19}F NMR (282 MHz, $CDCl_3$) δ –61.90 (dd, *J* = 15.3, 12.6 Hz), –63.48, –111.76 – –112.14 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, *J* = 17.3 Hz), 160.4 (d, *J* = 2.1 Hz), 158.2 (d, *J* = 17.3 Hz), 140.7 (d, *J* = 5.7 Hz), 139.8 – 139.2 (m), 138.4 (d, *J* = 6.1 Hz), 136.2 (d, *J* = 10.3 Hz), 135.8 – 134.4 (m), 134.0, 133.0, 132.8 (d, *J* = 6.6 Hz), 127.7 (ddt, *J* = 20.1, 9.0, 4.2 Hz), 126.8 (dd, *J* = 9.5, 4.2 Hz), 124.4, 123.4, 122.4 – 121.3 (m), 120.9 – 120.3 (m), 119.9 (dd, *J* = 22.1, 11.1 Hz), 69.3, 33.6, 25.8s; IR (Neat Film, NaCl) 2963, 2907, 2873, 1664, 1621, 1574, 1497, 1479, 1664, 1621, 1574, 1497, 1479, 1407, 1322, 1235, 1178, 1136, 1178, 1083, 1042, 964, 915, 833, 720, 699, 629 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{28}H_{22}F_{11}NO_2P$ $[M+H]^+$: 644.1207, found 644.1184.



(*S*)-2-(2-(bis(3-fluoro-4-(trifluoromethyl)phenyl)phosphaneyl)-5-(trifluoromethyl)phenyl)-4-(*tert*-butyl)-4,5-dihydrooxazole (*L2, (S)-Ty-PHOX*)

To an oven-dried 25 mL schlenk tube was added phosphine oxide **SI17** and Ph_2SiH_2 (1.49 mL, 8.05 mmol, 7.0 equiv) . The schlenk tube was then sealed and heated in a 140 ºC oil bath behind a blast shield. After 16 h, the reaction was cooled to 20 ºC and slowly opened to a nitrogen atmosphere. The colorless reaction mixture was then loaded directly onto a silica gel column (hexanes → 25% CH_2Cl_2 in hexanes) to provide a white foam (610 mg, 85% yield); $[\alpha]_D^{25}$ –12.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31–8.25 (m, 1H), 7.67–7.54 (m, 3H), 7.10 (dt, *J* = 19.3, 7.4 Hz, 2H), 7.03–6.95 (m, 3H), 4.33 (dd, *J* = 10.1, 8.7 Hz, 1H), 4.16 (t, *J* = 8.6 Hz, 1H),

3.99 (dd, J = 10.1, 8.5 Hz, 1H), 0.74 (s, 9H); ^{19}F NMR (282 Hz, $CDCl_3$) δ –61.51 (dd, J = 21.1, 12.4 Hz), –63.10, –113.31 – –113.52 (m), –113.57 – –113.78 (m); ^{31}P NMR (121 MHz, $CDCl_3$) δ –7.38; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.05 – 160.82 (m), 160.49 (d, J = 4.0 Hz), 158.46 – 158.25 (m), 145.63 (t, J = 4.2 Hz), 145.46 (d, J = 5.6 Hz), 140.49 (d, J = 28.6 Hz), 134.94, 134.74 – 134.58 (m), 134.47 – 134.20 (m), 132.38 (d, J = 20.4 Hz), 131.64 (q, J = 33.3 Hz), 129.24 (ddd, J = 34.0, 22.2, 3.7 Hz), 128.00 – 127.58 (m), 127.33 (dq, J = 12.2, 4.1 Hz), 126.65 (p, J = 3.4 Hz), 126.43, 124.79, 123.73, 122.44 – 120.79 (m), 119.75 – 118.09 (m), 68.83, 33.59, 25.60; IR (Neat Film, NaCl) 3071, 2960, 2871, 2138, 1655, 1617, 1570, 1491, 1430, 1403, 1323, 1176, 1133, 1083, 1042, 967, 830, 735, 714, 698, 684, 624 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{28}H_{22}F_{11}NOP$ $[M+H]^+$: 628.1258, found 628.1271.

X-Ray Crystal Structure for Allylated Product 2d (V18448)

An X-ray quality crystal of allylation product ***2d*** (compound V18448) was grown by slow evaporation of a solution in chloroform (approx. 30 mg/600 μL). Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound V18448. The structure was solved by direct methods using SHELXS[3] and refined against F^2 on all data by full-matrix least squares with SHELXL-2017[4] using established refinement techniques.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Compound V18448 crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit.

Figure S3. X-Ray Coordinate of Allylation Product *2d* (compound V18448)

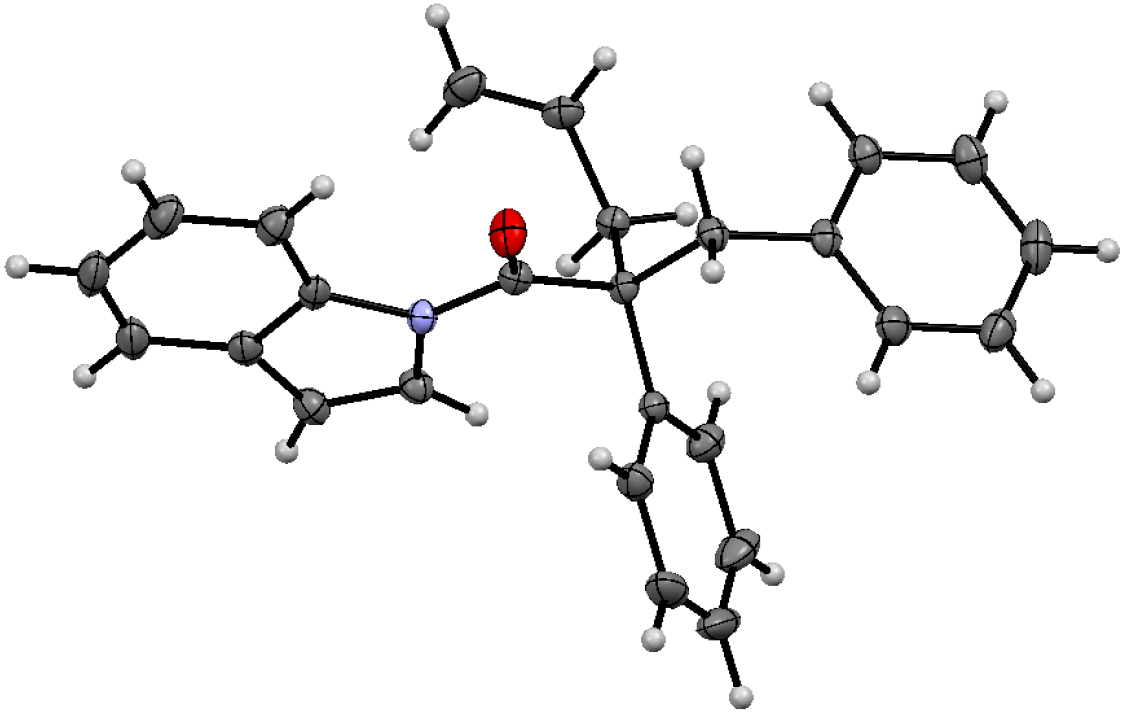


Table 1. Crystal data and structure refinement for V18448.

Identification code	v18448	
Empirical formula	C26 H23 N O	
Formula weight	365.45	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.2225(10) Å	a= 90°.
	b = 6.4382(6) Å	b= 99.6595(18)°.
	c = 14.0893(13) Å	g = 90°.
Volume	1003.56(16) $Å^3$	
Z	2	
Density (calculated)	1.209 Mg/m^3	
Absorption coefficient	0.564 mm^{-1}	
F(000)	388	
Crystal size	0.500 x 0.500 x 0.300 mm^3	
Theta range for data collection	3.182 to 80.104°.	
Index ranges	-14<=h<=14, -7<=k<=7, -17<=l<=17	

Reflections collected	34321
Independent reflections	4134 [R(int) = 0.0282]
Completeness to theta = 67.679°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8766
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4134 / 1 / 253
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0265, wR2 = 0.0681
R indices (all data)	R1 = 0.0265, wR2 = 0.0682
Absolute structure parameter	0.05(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.201 and -0.133 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for V18448. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5786(1)	1813(2)	7273(1)	26(1)
C(1)	5783(1)	3638(2)	7476(1)	17(1)
C(2)	4688(1)	5066(2)	7141(1)	15(1)
C(11)	4200(1)	5966(2)	8006(1)	17(1)
C(12)	4150(1)	4711(3)	8806(1)	24(1)
C(13)	3652(2)	5458(3)	9579(1)	35(1)
C(14)	3193(2)	7449(3)	9561(1)	37(1)
C(15)	3241(2)	8701(3)	8777(1)	34(1)
C(16)	3742(1)	7973(2)	8000(1)	24(1)
C(3)	3683(1)	3670(2)	6559(1)	18(1)
C(21)	2520(1)	4803(2)	6183(1)	18(1)
C(22)	1602(1)	4907(3)	6737(1)	24(1)
C(23)	530(1)	5950(3)	6403(1)	29(1)
C(24)	351(1)	6888(3)	5504(1)	30(1)
C(25)	1252(1)	6781(3)	4941(1)	27(1)
C(26)	2327(1)	5746(2)	5278(1)	21(1)
C(4)	5090(1)	6761(2)	6474(1)	17(1)
C(5)	5781(1)	5882(2)	5740(1)	22(1)
C(6)	6953(2)	6153(3)	5768(1)	29(1)
N(1)	6826(1)	4548(2)	7998(1)	17(1)
C(31)	6936(1)	6510(2)	8438(1)	20(1)
C(32)	8087(1)	6829(3)	8874(1)	23(1)
C(33)	8774(1)	5024(2)	8712(1)	21(1)
C(34)	9996(1)	4507(3)	8984(1)	27(1)
C(35)	10389(1)	2616(3)	8694(1)	31(1)
C(36)	9598(1)	1254(3)	8132(1)	31(1)
C(37)	8379(1)	1719(3)	7857(1)	24(1)
C(38)	7982(1)	3609(2)	8164(1)	18(1)

Table 3. Bond lengths [Å] and angles [°] for V18448.

O(1)-C(1)	1.2093(19)
C(1)-N(1)	1.4021(17)
C(1)-C(2)	1.5434(18)
C(2)-C(11)	1.5317(17)
C(2)-C(4)	1.5553(17)
C(2)-C(3)	1.5630(18)
C(11)-C(16)	1.390(2)
C(11)-C(12)	1.3950(19)
C(12)-C(13)	1.391(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.380(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.375(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.393(2)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(3)-C(21)	1.5111(18)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(21)-C(22)	1.3949(19)
C(21)-C(26)	1.3967(19)
C(22)-C(23)	1.388(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.387(2)
C(23)-H(23)	0.9500
C(24)-C(25)	1.388(2)
C(24)-H(24)	0.9500
C(25)-C(26)	1.390(2)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(4)-C(5)	1.5041(18)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900

C(5)-C(6)	1.320(2)
C(5)-H(5)	0.9500
C(6)-H(6A)	0.9500
C(6)-H(6B)	0.9500
N(1)-C(31)	1.4035(18)
N(1)-C(38)	1.4145(17)
C(31)-C(32)	1.3505(19)
C(31)-H(31)	0.9500
C(32)-C(33)	1.433(2)
C(32)-H(32)	0.9500
C(33)-C(34)	1.4006(19)
C(33)-C(38)	1.410(2)
C(34)-C(35)	1.380(3)
C(34)-H(34)	0.9500
C(35)-C(36)	1.395(3)
C(35)-H(35)	0.9500
C(36)-C(37)	1.391(2)
C(36)-H(36)	0.9500
C(37)-C(38)	1.390(2)
C(37)-H(37)	0.9500

O(1)-C(1)-N(1)	119.69(12)
O(1)-C(1)-C(2)	122.66(12)
N(1)-C(1)-C(2)	117.58(12)
C(11)-C(2)-C(1)	110.77(10)
C(11)-C(2)-C(4)	113.19(11)
C(1)-C(2)-C(4)	107.86(10)
C(11)-C(2)-C(3)	108.16(10)
C(1)-C(2)-C(3)	106.58(11)
C(4)-C(2)-C(3)	110.09(10)
C(16)-C(11)-C(12)	118.57(13)
C(16)-C(11)-C(2)	121.87(12)
C(12)-C(11)-C(2)	119.46(13)
C(13)-C(12)-C(11)	120.54(16)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7

C(14)-C(13)-C(12)	120.31(16)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	119.60(15)
C(15)-C(14)-H(14)	120.2
C(13)-C(14)-H(14)	120.2
C(14)-C(15)-C(16)	120.62(17)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(11)-C(16)-C(15)	120.36(15)
C(11)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(21)-C(3)-C(2)	114.28(11)
C(21)-C(3)-H(3A)	108.7
C(2)-C(3)-H(3A)	108.7
C(21)-C(3)-H(3B)	108.7
C(2)-C(3)-H(3B)	108.7
H(3A)-C(3)-H(3B)	107.6
C(22)-C(21)-C(26)	118.29(13)
C(22)-C(21)-C(3)	120.20(12)
C(26)-C(21)-C(3)	121.50(12)
C(23)-C(22)-C(21)	120.85(14)
C(23)-C(22)-H(22)	119.6
C(21)-C(22)-H(22)	119.6
C(24)-C(23)-C(22)	120.35(14)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	119.44(14)
C(23)-C(24)-H(24)	120.3
C(25)-C(24)-H(24)	120.3
C(24)-C(25)-C(26)	120.22(14)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-H(25)	119.9
C(25)-C(26)-C(21)	120.85(13)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6

C(5)-C(4)-C(2)	112.72(12)
C(5)-C(4)-H(4A)	109.0
C(2)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
C(2)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(6)-C(5)-C(4)	123.74(14)
C(6)-C(5)-H(5)	118.1
C(4)-C(5)-H(5)	118.1
C(5)-C(6)-H(6A)	120.0
C(5)-C(6)-H(6B)	120.0
H(6A)-C(6)-H(6B)	120.0
C(1)-N(1)-C(31)	127.69(12)
C(1)-N(1)-C(38)	124.72(12)
C(31)-N(1)-C(38)	107.59(11)
C(32)-C(31)-N(1)	110.11(13)
C(32)-C(31)-H(31)	124.9
N(1)-C(31)-H(31)	124.9
C(31)-C(32)-C(33)	107.67(13)
C(31)-C(32)-H(32)	126.2
C(33)-C(32)-H(32)	126.2
C(34)-C(33)-C(38)	119.61(15)
C(34)-C(33)-C(32)	132.62(15)
C(38)-C(33)-C(32)	107.76(12)
C(35)-C(34)-C(33)	118.44(15)
C(35)-C(34)-H(34)	120.8
C(33)-C(34)-H(34)	120.8
C(34)-C(35)-C(36)	121.20(14)
C(34)-C(35)-H(35)	119.4
C(36)-C(35)-H(35)	119.4
C(37)-C(36)-C(35)	121.68(16)
C(37)-C(36)-H(36)	119.2
C(35)-C(36)-H(36)	119.2
C(38)-C(37)-C(36)	116.98(15)
C(38)-C(37)-H(37)	121.5
C(36)-C(37)-H(37)	121.5

C(37)-C(38)-C(33)	122.06(13)
C(37)-C(38)-N(1)	131.03(13)
C(33)-C(38)-N(1)	106.87(12)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for V18448. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	23(1)	15(1)	39(1)	-3(1)	-1(1)	2(1)
C(1)	18(1)	16(1)	18(1)	1(1)	3(1)	-1(1)
C(2)	16(1)	14(1)	16(1)	0(1)	2(1)	1(1)
C(11)	14(1)	20(1)	16(1)	-2(1)	2(1)	-3(1)
C(12)	21(1)	31(1)	21(1)	4(1)	3(1)	-2(1)
C(13)	27(1)	59(1)	19(1)	1(1)	6(1)	-9(1)
C(14)	26(1)	60(1)	27(1)	-19(1)	13(1)	-9(1)
C(15)	28(1)	34(1)	43(1)	-17(1)	15(1)	-2(1)
C(16)	24(1)	23(1)	28(1)	-4(1)	8(1)	0(1)
C(3)	18(1)	17(1)	20(1)	-1(1)	1(1)	-1(1)
C(21)	16(1)	15(1)	22(1)	-2(1)	1(1)	-2(1)
C(22)	20(1)	28(1)	24(1)	-2(1)	2(1)	-5(1)
C(23)	18(1)	32(1)	37(1)	-7(1)	7(1)	-2(1)
C(24)	17(1)	25(1)	46(1)	-1(1)	-2(1)	2(1)
C(25)	23(1)	23(1)	32(1)	6(1)	-3(1)	-2(1)
C(26)	18(1)	22(1)	24(1)	0(1)	1(1)	-3(1)
C(4)	18(1)	16(1)	17(1)	2(1)	3(1)	0(1)
C(5)	28(1)	22(1)	19(1)	1(1)	7(1)	0(1)
C(6)	30(1)	33(1)	28(1)	8(1)	13(1)	7(1)
N(1)	16(1)	15(1)	19(1)	1(1)	2(1)	1(1)
C(31)	20(1)	18(1)	20(1)	-2(1)	1(1)	0(1)
C(32)	22(1)	24(1)	21(1)	-1(1)	0(1)	-3(1)
C(33)	19(1)	27(1)	17(1)	4(1)	3(1)	-2(1)
C(34)	17(1)	40(1)	24(1)	6(1)	1(1)	0(1)
C(35)	17(1)	44(1)	31(1)	10(1)	5(1)	7(1)
C(36)	26(1)	33(1)	34(1)	7(1)	10(1)	11(1)
C(37)	23(1)	24(1)	27(1)	3(1)	6(1)	4(1)
C(38)	15(1)	22(1)	17(1)	6(1)	4(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for V18448.

	x	y	z	U(eq)
H(12)	4458	3335	8822	29
H(13)	3627	4594	10122	42
H(14)	2846	7953	10087	45
H(15)	2929	10074	8765	41
H(16)	3771	8853	7463	29
H(3A)	3999	3053	6008	22
H(3B)	3503	2516	6978	22
H(22)	1710	4257	7351	29
H(23)	-83	6021	6792	34
H(24)	-384	7599	5275	36
H(25)	1134	7416	4324	32
H(26)	2939	5680	4887	26
H(4A)	4365	7493	6137	20
H(4B)	5602	7793	6874	20
H(5)	5351	5085	5227	27
H(6A)	7407	6943	6273	35
H(6B)	7341	5559	5284	35
H(31)	6293	7474	8431	24
H(32)	8389	8032	9225	27
H(34)	10541	5436	9358	33
H(35)	11213	2235	8880	37
H(36)	9901	-24	7933	37
H(37)	7842	786	7476	29

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