SUPPORTING INFORMATION

Synthesis of 2-Aryl and 2-Vinylpyrrolidines via Copper-catalyzed Coupling of Styrenes and Dienes with Potassium β-Aminoethyltrifluoroborates

Chanchamnan Um and Sherry R. Chemler

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14226, United States

schemler@buffalo.edu

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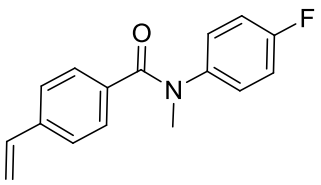
General Experimental Information:

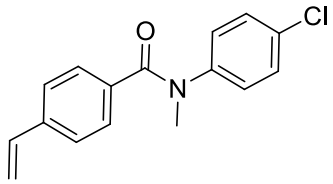
All reagents were used out of the bottle as purchased from the supplier without further purification unless otherwise noted. ^{1}H NMR spectra were recorded in $CDCl_3$ (using 7.26 ppm for reference of $CHCl_3$) at 300, 400 or 500 MHz unless otherwise noted. ^{13}C NMR spectra were recorded in $CDCl_3$ (using 77.0 ppm as internal reference) at 75.5 MHz unless otherwise noted. IR spectra were taken neat using a Nicolet-Impact 420 FTIR. Wave numbers in cm^{-1} are reported for characteristic peaks. High resolution mass spectra were obtained at SUNY Buffalo's mass spec. facility on a ThermoFinnigan MAT XL spectrometer. Bis(trifluoromethylsulfonyloxy)copper, 1,10-phenanthroline, were purchased from Acros. Potassium (2-(*tert*-butoxycarbonylamino)ethyl) trifluoroborate salt and potassium benzyl N-[2-(trifluoroboran-uidyl)ethyl]carbamate salt and potassium (2-(*tert*-butoxycarbonylamino)ethyl) trifluoroborate salt were purchased from Frontier Scientific. Activated manganese(IV) oxide (MnO_2, ~85% purity, <5μm) was purchased from Aldrich and used without further purification. 4-Methoxy styrene, ethene-1,1-diyldibenzene, prop-1-en-2-ylbenzene, 4-chloro styrene and 4Å molecular sieves (<50 μm) were purchased from Acros and used without further purification. 2-Methoxy-styrene, 4-methyl styrene, 4-*tert*-butyl styrene, and 1H-indene were purchased from Aldrich and used without further purification. 4-Vinyl-benzoic acid, 1-fluoro-4-vinylbenzene and 1-bromo-4-vinylbenzene were purchased from Alfa Aesar and used without further purification. Bexarotene (free acid) was purchased from LC laboratories. The following known alkenes were synthesized using published procedures:1-methoxy-3-vinylbenzene[1], 5-vinylbenzo[d][1,3]dioxole[2], 1,2-dimethoxy-4-vinylbenzene[3], 4-vinylbiphenyl[4], 7-vinyl-1H-indole[5], 3-methylene-2,3-dihydrobenzofuran[6], (E)-deca-1,3-diene[7], (E)-buta-1,3-dienylbenzene[8], 1-methoxy-4-(prop-1-en-2-yl)benzene[9], 1-methy[6]lene-1,2,3,4-tetrahydronaph-thalene[10], (2E,4E)-methyl 5-(benzo[d][1,3]dioxol-5-yl)penta-2,4-dienoate[11]. 4Å Molecular sieves (<50 μm) were flamed activated before addition to the reaction mixture.

Synthesis of novel alkenes



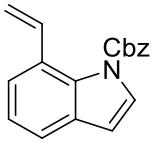
***N*-(4-fluorophenyl)-4-vinylbenzamide**

To a 50 mL round-bottomed flask, 4-vinylbenzoic acid (296 mg, 2.0 mmol, 1.0 equiv.) and hydroxybenzotriazole (HOBT) (324 mg, 2.4 mmol, 1.2 equiv.) was dissolved in 10 mL of anhydrous DCM under Ar. After 5 minutes, diisopropyl ethylamine (DIPEA) (1.8 mL, 6.0 mmol, 3.0 equiv.) and 4-fluoro-*N*-methylaniline (257 mg, 2.2 mmol, 1.1 equiv.) were added to the mixture respectively. The mixture was stirred at RT until it turned homogeneous. To the stirring clear solution, *N,N′*-diisopropyl carbodiimide (DIC) (277 mg, 2.2 mmol, 1.1 equiv.) was added and the reaction was allowed to stirred at RT overnight. Upon completion, the reaction was diluted with 50 mL EtOAc and washed with 30 mL of saturated aq. $NaHCO_3$. The aqueous phase was extracted with EtOAc (30 mL x 3). The combined organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The crude oil was purified by using flash column chromatography on SiO_2 (10% EtOAc:hexanes) to give *N*-(4-fluorophenyl)-4-vinylbenzamide (260 mg, 51%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.17 (m, 4H), 7.05 – 6.98 (m, 2H), 6.97 – 6.87 (m, 2H), 6.61 (dd, J = 17.6, 10.9 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.26 (dd, J = 10.9, 0.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 159.5, 141.0, 138.8, 136.0, 134.8, 129.0, 128.5, 128.4, 125.6, 116.2, 116.0, 115.3, 38.6; IR neat film: 2927, 1702, 1641, 1508, 848, 700 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{15}O_1N_1F_1]^+$: 256.1143 found 256.1140.



_N_-(4-chlorophenyl)-4-vinylbenzamide

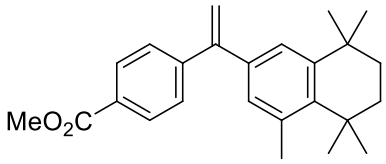
_N_-(4-chlorophenyl)-4-vinylbenzamide was synthesized from 4-chloro-_N_-methylaniline (155 mg, 1.1 mmol, 1.1 equiv.) and 4-vinyl benzoic acid (148 mg, 1.0 mmol, 1.0 equiv.) using the same procedure as described above. _N_-(4-chlorophenyl)-4-vinylbenzamide was purified by using flash column chromatography on SiO_2 (10% EtOAc:hexanes) to give _N_-(4-chlorophenyl)-4-vinylbenzamide (165 mg, 61%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 - 7.23 (m, 4 H), 7.20 (d, J = 9.0 Hz, 2 H), 6.98 (d, J = 8.6 Hz, 2 H), 6.63 (dd, J = 10.9, 17.5 Hz, 1 H), 5.73 (d, J = 17.5 Hz, 1 H), 5.28 (d, J = 11.3 Hz, 1 H), 3.47 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 143.2, 138.6, 135.6, 134.4, 131.6, 129.0, 128.8, 127.7, 125.4, 115.2, 38.0; IR neat film: 3086, 1740, 1645, 1492, 1358, 1102, 835, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{15}O_1N_1Cl_1]^+$: 272.0848 found 272.0838.



Benzyl 7-vinyl-1H-indole-1-carboxylate

To a 50 mL round-bottomed flask 7-vinyl-1H-indole (143 mg, 1.0 mmol, 1.0 equiv.) was dissolved in 10 mL of DMSO:DME (1:10) and cooled to 0 °C followed by addition of NaH (25 mg, 1.1 mmol, 1.1 equiv., 99%) and stirred for 30 min. Benzyl chloroformate (204 mg, 1.2 mmol, 1.2 equiv.) was then added and the reaction was allowed to warm to room temperature and was stirred overnight. Upon completion, the reaction was diluted with 50 mL EtOAc and washed with 30 mL of saturated aq. $NaHCO_3$. The aqueous phase was extracted with EtOAc (30 mL x 3). The combined organic phase

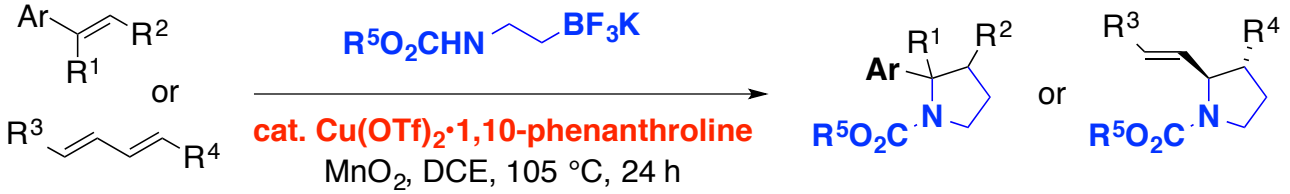
was dried over Na_2SO_4 and concentrated in *vacuo*. The crude oil was purified by using flash column chromatography on SiO_2 (10% EtOAc:hexanes) to give benzyl 7-vinyl-1H-indole-1-carboxylate as colorless oil (227 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 3.9 Hz, 1 H), 7.53 - 7.31 (m, 9 H), 7.26 - 7.22 (m, 1 H), 6.58 (d, *J* = 3.9 Hz, 1 H), 5.56 (dd, *J* = 1.6, 17.5 Hz, 1 H), 5.41 (s, 2 H), 5.23 (dd, *J* = 1.4, 10.7 Hz, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 137.0, 135.0, 132.1, 128.7, 128.6, 127.8, 126.8, 124.5, 123.7, 120.5, 113.0, 108.4, 68.9; IR neat film: 3066, 2957, 1746, 1409, 1316, 729 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{15}O_2N_1Na_1]^+$: 300.1006 found 300.0994.



Methyl 4-(1-(4,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (Bexarotene methyl ester)

In a 10 mL oven-dried round bottom flask, bexarotene free acid (178.7 mg, 0.5 mmol, 1.0 equiv.) and anhydrous potassium carbonate (345 mg, 2.5 mmol, 5.0 equiv.) were dissolved in anhydrous acetone (2 mL) under Ar. Methyl iodide (85 μL, 0.6 mmol, 1.2 equiv.) was added at RT. The reaction was allowed to stir at that temperature overnight. The solid was filtered and washed with anhydrous acetone (10 mL). The combined organic phase was concentrated in vacuo to give a crude oil which was purified over silica gel (20% EtOAc:hexanes) to give bexarotene methyl ester (178.7 mg, 99%) as pale yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.95 (d, *J*=8 Hz, 2 H) 7.34 (d, *J*=9 Hz, 2 H) 7.12 (s, 1 H) 7.07 (s, 1 H) 5.81 (d, *J*=1 Hz, 1 H) 5.32 (s, 1 H) 3.91 (s, 3 H) 1.94 (s, 3 H) 1.70 (s, 4 H) 1.30 (s, 6 H) 1.27 (s, 6 H). This data matched the data reported for this compound.[12]

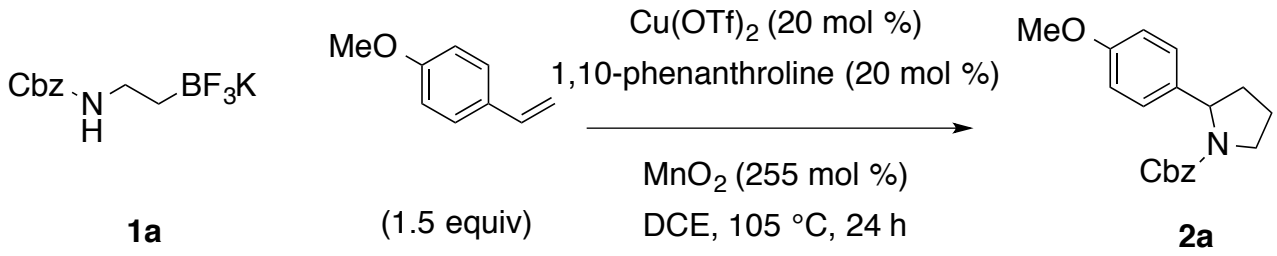
General procedure for copper-catalyzed oxidative coupling between alkenes and β−aminoethyltrifluoroborate



Ar = benzene and pyridine derivatives, indoles
R^{1-4} = H, alkyl, aryl, CO_2R, alkynyl; R^5 = Bn or *t*-Bu

$Cu(OTf)_2$ (20 mol%) was placed in a glass pressure tube, under an argon atmosphere. The $Cu(OTf)_2$ was gently flamed-dried under vacuum then back-filled with argon for 3 times. The tube was allowed to reach ambient temperature before adding an oven-dried stir bar and a freshly prepared solution of 1,10-phenanthroline (25 mol%) in anhydrous DCE, added via syringe through a Teflon septum. The tube was capped and the reaction mixture was placed in a 60 ˚C oil bath and stirred. After 2 hours, the catalyst solution was cooled to ambient temperature and the solid potassium trifluoroborate **1** (1 equiv.) and solid MnO_2 (2.55 equiv based on 85% purity) were added under argon followed by the addition of solution of alkene (1.5 – 2.5 equiv.) in anhydrous DCE. The mixture was sonicated for a few seconds and then placed in a 105 ˚C oil bath and stirred. After the noted time (28 – 48 h), the reaction mixture was cooled to ambient temperature, diluted with EtOAc (*ca.* 10 mL), sonicated and filtered through a short pad of silica gel. The silica gel was washed with additional EtOAc (150 - 250 mL), and the organic mixture was concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel as described below.

Representative coupling protocol:

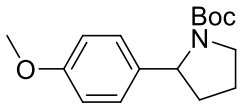


1a (1.5 equiv) **2a**

(±)-Benzyl 2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (2a)

$Cu(OTf)_2$ (9.0 mg, 0.025 mmol, 20 mol%,) was placed in a glass pressure tube, under an argon atmosphere. The $Cu(OTf)_2$ was flamed dried under vacuum then back filled with argon for 3 times. The tube was allowed to reach ambient temperature before a freshly prepared solution of 1,10-phenanthroline (5.6 mg, 0.031 mmol, 25 mol%) in anhydrous DCE was added via syringe through a teflon septum. A magnetic stir bar was added and the tube was capped. The reaction mixture was placed in a 60 ˚C oil bath and stirred. After 2 hours, the catalyst solution was cooled to ambient temperature and the solid Potassium benzyl *N*-[2-(trifluoroboranuidyl)ethyl]carbamate (**1**) (37.1 mg, 0.13 mmol, 1.00 equiv.) and solid MnO_2 (32.6 mg, 0.38 mmol, 2.55 equiv. based on 85% purity) were added under argon followed by the addition of a solution of 4-methoxy styrene (25.2 mg, 0.19 mmol, 1.50 equiv.) in anhydrous DCE. The mixture was sonicated for a few seconds and then placed in a 105 ˚C oil bath and stirred. After the noted time 24 h, the reaction mixture was cooled to ambient temperature, diluted with EtOAc (*ca.* 10 mL), sonicated and filtered through a short pad of silica gel. The silica gel was washed with additional EtOAc (150 - 250 mL), and concentrated *in vacuo*. The crude was purified by flash chromatography on silica gel (10 – 11% EtOAc/hexanes gradient) to give title product **2a** (32.0 mg, 82%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.45 - 7.28 (m, 2 H), 7.23 - 7.01 (m, 3 H), 6.94 (brs, 1 H), 6.83 (d, J = 7.4 Hz, 2 H), 5.22 -

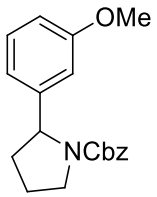
4.82 (m, 3 H), 3.80 (brs, 3 H), 3.73 - 3.54 (m, 2 H), 2.37 - 2.20 (m, 1 H), 2.02 - 1.75 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 158.4, 155.1, 136.8, 136.4, 135.7, 128.4, 128.1, 127.8, 127.4, 127.3, 126.6, 113.7, 66.5, 60.7, 60.5, 55.3, 47.5, 47.1, 35.9, 34.7, 23.6, 22.9; ^{13}C NMR (101 MHz, $CDCl_3$, 50 ˚C) rotomeric mixture: δ 158.6, 155.0, 137.1, 136.1, 128.2, 127.6, 126.6, 113.9, 66.6, 60.7, 55.3, 47.5, 35.7, 23.2; IR neat thin film: 2954, 2928, 1696, 1512, 1411, 1352, 1245, 738, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_3N_1]^+$: 312.1594 found 312.1595.



(±)-Benzyl 2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (2b)[13]

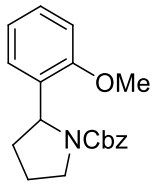
Following the general procedure, **2b** was obtained from 4-methoxy styrene (25.2 mg, 0.19 mmol, 1.50 equiv.) and potassium (2-(tert-butoxycarbonylamino)ethyl) trifluoroborate salt (31.4 mg, 0.13 mmol, 1.00 equiv.) after 24 h stirring at 105 ˚C. The product **2b** (16.1 mg, 46%) was isolated as colorless oil after flash column chromatography on silica gel (10–11% EtOAc/hexanes gradient). The ^{1}H NMR at ambient temperature agreed with the reported spectra.[13] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): rotomeric mixture δ 7.08 (d, *J* = 8.2 Hz, 2 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 4.89 and 4.72 (2 brs, 1H), 3.79 (s, 3 H), 3.49 - 3.67 (m, 2H), 2.36 - 2.17 (m, 1 H), 2.00 - 1.69 (m, 3 H), 1.44 (brs, 3 H), 1.31 - 1.08 (brs, 6 H). ^{1}H NMR (400 MHz, $CDCl_3$, 50 ˚C): δ 7.08 (d, *J* = 8.6 Hz, 2 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 4.90 - 4.65 (m, 1 H), 3.79 (s, 3 H), 3.49 - 3.67 (m, 2H), 2.36 - 2.17 (m, 1 H), 2.00 - 1.71 (m, 3 H), 1.27 (brs, 9 H).

Note: The ^{1}H NMR spectra recorded at -20 ˚C published by Campos et al (2006)[14] showed that the rotomeric peaks were clearly resolved while the same peaks from the same compound appearing on the spectra at ambient temperature, published by Doyle & MacMillan et al (2014)[15], were not as clearly resolved. This shows that by varying the temperature, the equilibrium between the two rotomers is affected. This phenoma is also reported by Ley et. al (2012).[16] The authors claim that variable-temperature (VT) NMR technique can be used to distinguish equilibrating species such as rotomers from non-equilibrating diastereomers. In our case, by recording the ^{1}H NMR NMR spectra at 50 ˚C, the rotomeric peaks were combined to form a single peak indicating that the 2 signals at 4.89 ppm and 4.72 ppm were rotomeric. The same phenomena can also be observed for the peaks 1.44 and 1.08 ppm that combines to form a broad singlet at 1.27 ppm.



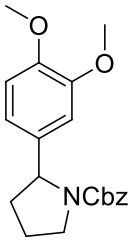
(±)-Benzyl 2-(3-methoxyphenyl)pyrrolidine-1-carboxylate (2c)

Following the representative procedure, **2c** was obtained from 3-methoxystyrene (33.6 mg, 0.25 mmol, 2 equiv.) after 24 h stirring at 105 °C. The product **2c** (26.5 mg, 68%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.49 - 7.10 (m, 5 H), 6.94 (brs, 1 H), 6.85 - 6.62 (m, 3 H), 5.24 - 4.85 (m, 3 H), 3.88 - 3.52 (m, 5 H), 2.39 - 2.21 (m, 1 H), 2.02 - 1.78 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 159.7, 155.0, 146.1, 145.3, 136.7, 129.4, 128.4, 128.1, 127.9, 127.4, 127.3, 117.8, 112.0, 111.8, 111.5, 111.2, 66.7, 66.5, 61.2, 61.0, 55.1, 47.6, 47.1, 35.8, 34.7, 23.5, 22.9; IR neat thin film: 2948, 1698, 1600, 1585, 1408, 1256, 1198, 770, 697 cm^{-1}; HRMS (EI) calcd for [$C_{19}H_{22}O_3N_1$]: 311.1516 found 311.1517.



(±)-Benzyl 2-(2-methoxyphenyl)pyrrolidine-1-carboxylate (**2d**)

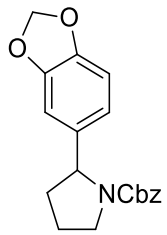
Following the general procedure, **2d** was obtained from 2-methoxy styrene (33.6 mg, 0.25 mmol, 2 equiv.) after 48 h stirring at 105 °C. The product **2d** (26.1 mg, 67%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ 7.46 - 7.29 (m, 2 H), 7.26 - 7.11 (m, 2 H), 7.03 (t, J = 9.0 Hz, 1 H), 6.98 - 6.80 (m, 3 H), 5.34 - 5.21 (m, 1 H), 5.21 - 4.89 (m, 2 H), 3.88 - 3.75 (m, 3 H), 3.75 - 3.51 (m, 2 H), 2.27 (d, J = 8.2 Hz, 1 H), 1.85 (d, J = 4.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 156.0, 155.0, 154.6, 137.1, 137.0, 132.2, 131.3, 128.4, 127.9, 127.6, 127.3, 125.8, 125.4, 120.3, 120.2, 110.3, 66.6, 66.3, 56.8, 56.1, 55.3, 47.5, 47.1, 33.8, 32.8, 23.3, 22.8; IR (neat film): 2928, 1702, 1489, 1411, 1351, 1244, 1104, 1116, 753, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_3N_1]^+$: 312.1594 found 312.1593.



(±)-Benzyl 2-(3,4-dimethoxyphenyl)pyrrolidine-1-carboxylate (**2e**)

Following the representative procedure, **2e** was obtained from 3,4-dimethoxy styrene (40.1 mg, 0.25 mmol, 2.0 equiv.) after 24 h stirring at 105 °C. The product **2e** (26.9 mg, 63%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 25% EtOAc/hexanes gradient).

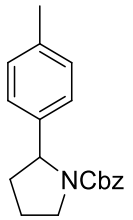
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.46 - 7.14 (m, 5 H), 6.95 (brs, 1 H), 6.87 - 6.54 (m, 3 H), 5.22 - 4.76 (m, 3 H), 3.96 - 3.55 (m, 8 H), 2.41 - 2.18 (m, 1 H), 2.04 - 1.80 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 155.1, 148.9, 147.8, 137.0, 128.1, 127.9, 127.5, 127.4, 117.4, 111.1, 108.9, 66.6, 60.8, 55.9, 55.8, 47.6, 47.1, 35.9, 34.7, 23.6, 23.0; IR neat film: 2939, 1697, 1514, 767, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{24}O_4N_1]^+$:342.1711 found 342.1705.



(±)-Benzyl 2-(benzo[d][1,3]dioxol-5-yl)pyrrolidine-1-carboxylate (**2f**)

Following the representative procedure, **2f** was obtained from 5-vinylbenzo[d][1,3]dioxole (55.5 mg, 0.38 mmol, 1.5 equiv.) after 24 h stirring at 105 °C. The product **2f** (62.6 mg, 77%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 25% EtOAc/hexanes gradient). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.57 - 7.12 (m, 3 H), 7.00 (br.s, 1 H), 6.91 - 6.53 (m, 2 H), 6.10 - 5.82 (m, 2 H), 5.31 - 4.77 (m, 3 H), 3.78 - 3.54 (m, 2 H), 2.43 - 2.16 (m, 1 H), 2.11 - 1.77 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 154.9, 147.7, 146.3, 138.4, 137.6, 136.9, 136.7, 128.4, 128.1, 127.8, 127.5, 127.3, 118.5, 108.1, 108.0, 106.1, 100.9, 66.7, 66.5, 61.1, 60.8, 47.5, 47.1, 35.9, 34.8, 23.5, 22.8; ^{13}C NMR (126 MHz, $CDCl_3$, 60 °C): δ 155.0, 147.8, 146.4, 138.4, 137.0, 128.2, 127.6, 118.7, 108.1, 106.2, 100.9, 66.7, 61.1, 47.4, 35.6, 23.2; IR neat thin film: 2971, 2950, 2881, 1698, 1487, 1409, 1353, 1235, 1036, 771, 697 cm^{-1}; HRMS (EI) calcd for [$C_{19}H_{19}O_4N_1$]: 325.1309 found 325.1310.

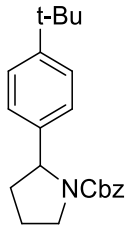
Ten-Fold Scale Reaction: Following the representative procedure, **2f** was obtained from 5-vinylbenzo[d][1,3]dioxole (280 mg, 1.88 mmol, 1.5 equiv) and alkyltrifluoroborate **1a** (356 mg, 1.25 mmol) after 24 h stirring at 105 °C. The product **2f** (285 mg, 70%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 25% EtOAc/hexanes gradient).



(±)-Benzyl 2-p-tolylpyrrolidine-1-carboxylate (2g)

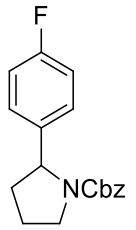
Following the representative procedure, **2g** was obtained from 4-methyl styrene (29.5 mg, 0.25 mmol, 2.0 equiv.) after 24 h stirring at 105 °C. The product **2g** (22.6 mg, 61%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.52 - 6.77 (m, 8 H), 5.26 - 4.83 (m, 3 H), 3.78 - 3.46 (m, 2 H), 2.48 - 2.17 (m, 4 H), 2.05 - 1.76 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture δ: 155.0, 141.3, 140.5, 137.0, 136.8, 136.2, 129.0, 128.4, 128.1, 127.9, 127.4, 127.2, 125.4, 66.4, 61.1, 60.8, 47.6, 47.1, 35.9, 34.8, 23.6, 22.8, 21.0; IR neat thin film: 2963, 1701, 1409, 1259, 1079, 1017, 765, 797, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2N_1]$: 296.1645 found 296.1654.



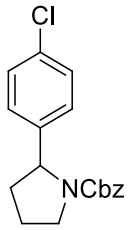
(±)-Benzyl 2-(4-tert-butylphenyl)pyrrolidine-1-carboxylate (**2h**)

Following the representative procedure, (**2h**) was obtained from 4-tert-butyl styrene (40.0 mg, 0.25 mmol, 2.00 equiv.) after 24 h stirring at 105 °C. The product (**2h)** (28.7mg, 68%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.49 - 7.28 (m, 4 H), 7.21 - 7.01 (m, 4 H), 6.86 (d, *J* = 6.2 Hz, 1 H), 5.29 - 4.85 (m, 3 H), 3.81 - 3.55 (m, 2 H), 2.20 - 2.10 (m, 1 H), 2.06 - 1.68 (m, 3 H), 1.36 - 1.24 (m, 9); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 155.0, 149.5, 141.2, 140.3, 137.1, 136.8, 128.4, 128.0, 127.9, 127.4, 127.2, 125.8, 125.2, 66.5, 60.8, 47.6, 47.1, 35.8, 34.6, 34.4, 31.4, 23.6, 22.9; IR neat thin film: 2961, 1702, 1410, 1353, 1261, 1103, 797, 696 cm^{-1}; HRMS (ESI) calcd for $[C_{22}H_{28}O_2N_1]^+$: 338.2115 found 338.2122.



(±)-Benzyl 2-(4-fluorophenyl)pyrrolidine-1-carboxylate (2i)

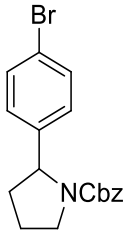
Following the representative procedure, **2i** was obtained from 4-fluoro styrene (30.5 mg, 0.25 mmol, 2.0 equiv.) after 36 h stirring at 105 °C. The product **2i** (19.5 mg, 52%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ: 7.61 - 7.29 (m, 3 H), 7.24 - 6.83 (m, 6 H), 5.23 - 4.81 (m, 3 H), 3.79 - 3.53 (m, 2 H), 2.40 - 2.19 (m, 1 H), 2.00 - 1.72 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ: 163.3, 160.1, 154.9, 140.0, 139.2, 136.9, 136.6, 128.4, 128.2, 127.9, 127.6, 127.4, 127.1, 127.0, 115.3, 115.0, 66.6, 60.7, 60.5, 47.6, 47.1, 35.9, 34.8, 23.6, 22.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.6 ppm; IR neat thin film: 2954, 1702, 1604, 1509, 1411, 1353, 1222, 1111, 830, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{19}O_2N_1F_1]^+$: 300.1394 found 300.1400.



(±)-Benzyl 2-(4-chlorophenyl)pyrrolidine-1-carboxylate (2j)

Following the representataive procedure, **2j** was obtained from p-chloro styrene (34.5 mg, 0.25 mmol, 2.0 equiv.) after 36 h stirring at 105 °C. The product **2j** (29.6 mg, 75%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient).

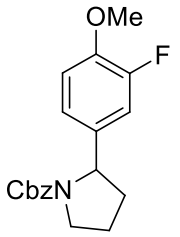
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ: 7.45 - 7.27 (m, 2 H), 7.25 - 7.00 (m, 4 H), 6.98 - 6.82 (m, 1 H), 5.20 - 4.81 (m, 3 H), 3.74 - 3.55 (m, 2 H), 2.41 - 2.21 (m, 1 H), 2.00 - 1.74 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ: 154.9, 142.9, 142.1, 137.4, 136.9, 136.5, 132.4, 128.5, 128.2, 127.9, 127.6, 127.4, 126.9, 66.7, 60.8, 60.6, 47.6, 47.2, 35.9, 34.7, 23.6, 22.9; IR neat thin film: 2927, 1700, 1490, 1409, 1352, 1090, 1013, 821, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{19}O_2N_1Cl_1]^+$: 316.1099 found 316.1101.



(±)-Benzyl 2-(4-bromophenyl)pyrrolidine-1-carboxylate (2k)

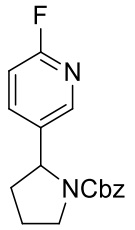
Following the representative procedure, **2k** was obtained from 4-bromo styrene (45.8 mg, 0.25mmol, 2.0 equiv.) after 48 h stirring at 105 °C. The product **2k** (25.1 mg, 56%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.49 - 7.27 (m, 4 H), 7.23 - 7.16 (m, 2 H), 7.14 - 6.97 (m, 2 H), 6.97 - 6.85 (m, 1 H), 5.20 - 4.80 (m, 3 H), 3.73 - 3.57 (m, 2 H), 2.41 - 2.24 (m, 1 H), 1.97 - 1.74 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 155.0, 143.4, 142.6, 141.0, 140.9, 139.7, 137.0, 136.7, 128.7, 128.4, 128.1, 127.9, 127.4, 127.0, 125.9, 66.7, 66.5, 61.1, 60.9, 47.6, 47.2, 35.9, 34.7, 23.6, 23.0; IR neat thin film: 2967, 1700, 1487, 1408, 1352, 818, 696 cm^{-1}; HRMS (EI) calcd for [$C_{18}H_{18}O_2N_1Br_1$]: 359.0515 found 359.0517.



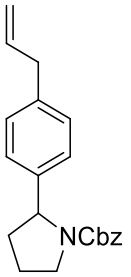
(±)-Benzyl 2-(3-fluoro-4-methoxyphenyl)pyrrolidine-1-carboxylate (2l)

Following the representative procedure, **2l** was obtained from 2-fluoro-1-methoxy-4-vinylbenzene (38 mg, 0.25 mmol, 2.0 equiv.) after 24 h stirring at 105 °C. The product **2l** (23.1 mg, 56%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 25% EtOAc/hexanes gradient). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.54 - 7.12 (m, 4 H), 7.09 - 6.71 (m, 4 H), 5.26 - 4.74 (m, 3 H), 3.88 (brs., 2 H), 3.86 (brs., 1 H), 3.76 - 3.51 (m, 2 H), 2.41 - 2.19 (m, 1 H), 2.01 - 1.75 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 154.9, 153.9, 150.7, 146.3, 146.2, 137.5, 136.8, 136.6, 128.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.6, 127.3, 121.1, 121.0, 113.5, 113.4, 113.3, 66.7, 66.6, 60.5, 60.2, 56.3, 47.5, 47.0, 35.7, 34.6, 23.5, 22.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -135.1 ppm; IR neat film: 2950, 1700, 1517, 1409, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{21}O_3N_1F_1]$: 330.1500 found 330.1503.



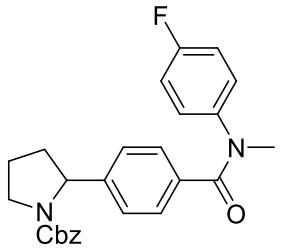
(±)-Benzyl 2-(6-fluoropyridin-3-yl)pyrrolidine-1-carboxylate (2m)

Following the representative procedure, **2m** was obtained from 2-fluoro-5-vinylpyridine (30.1 mg, 0.25 mmol, 2.00 equiv.) after 48 h, stirring at 95 °C. The product **2m** (13.1 mg, 35%) was isolated as yellow oil after flash column chromatography on silica gel (10-11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 8.15 - 7.94 (m, 1 H), 7.66 - 7.46 (m, 1 H), 7.42 - 7.16 (m, 4 H), 7.09 - 6.74 (m, 2 H), 5.20 - 4.80 (m, 3 H), 3.77 - 3.55 (m, 2 H), 2.37 (br. s., 1 H), 2.00 - 1.76 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 163.9, 154.8, 145.2, 145.0, 142.0, 138.7, 138.4, 136.5, 128.3, 127.9, 127.7, 109.3, 109.0, 67.0, 58.7, 58.3, 47.6, 47.1, 35.8, 34.5, 23.7, 23.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.0 ppm; IR, neat film: 2955, 1700, 1597, 1483, 1408, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{17}O_2N_2Na_1F_1]^+$: 323.1177 found 323.1170.



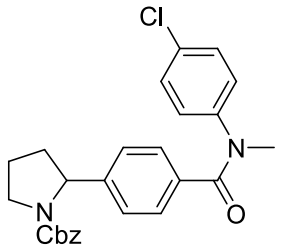
(±)-Benzyl 2-(4-allylphenyl)pyrrolidine-1-carboxylate (2n)

Following the representative procedure, **2n** was obtained from 1-allyl-4-vinylbenzene (36.1, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 °C. The product **2n** (20.5 mg, 51%) was isolated as colorless oil after flash column chromatography on silica gel (10 - 11 % EtOAc /hexanes gradient). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.48 - 7.01 (m, 8 H), 6.99 - 6.74 (m, 1 H), 6.08 - 5.87 (m, 1 H), 5.23 - 4.85 (m, 4 H), 3.77 - 3.55 (m, 2 H), 3.38 (d, *J* = 6.2 Hz, 2 H), 2.39 - 2.19 (m, 1 H), 2.04 - 1.72 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 155.0, 142.1, 141.3, 138.4, 137.5, 137.0, 136.8, 128.5, 128.1, 127.9, 127.4, 127.2, 126.1, 125.6, 115.7, 66.5, 61.0, 60.8, 47.6, 47.1, 39.8, 35.9, 34.7, 23.6, 22.9; IR neat film: 2978, 1702, 1409, 1352, 1009, 771, 661 cm^{-1}; HRMS (EI) calcd for [$C_{21}H_{23}O_2N_1$]: 321.1727 found 321.1723.



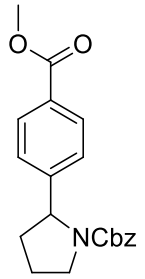
(±)-Benzyl 2-(4-((4-fluorophenyl)(methyl)carbamoyl)phenyl)pyrrolidine-1-carboxylate (2o)

Following the representative procedure, **2o** was obtained from *N*-(4-fluorophenyl)-*N*-methyl-4-vinylbenzamide (63.8 mg, 0.25 mmol, 2.0 equiv.) after 48 h, stirring at 105 °C. The product **2o** (28.1 mg, 52%) was isolated as colorless oil after flash column chromatography on silica gel (20 – 50% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.54 - 7.11 (m, 6 H), 7.10 - 6.62 (m, 7 H), 5.22 - 4.76 (m, 3 H), 3.71 - 3.52 (m, 2 H), 3.48 (br. s, 3 H), 2.36 - 2.14 (m, 1 H), 1.95 - 1.67 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 170.3, 162.4, 159.1, 154.9, 146.2, 145.4, 141.3, 141.0, 136.8, 136.5, 134.2, 134.0, 128.9, 128.5, 128.4, 128.2, 127.9, 127.6, 127.2, 125.4, 125.0, 116.2, 115.9, 66.6, 60.8, 47.6, 47.0, 38.6, 35.7, 34.5, 23.4, 22.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.9 ppm; IR neat film: 2922, 2851, 2649, 2286, 2324, 1703, 1647, 1576, 1492, 1413, 1392, 753 cm^{-1}; HRMS (EI) calcd for [$C_{26}H_{25}O_3N_1F_1$]: 432.1841 found 432.1844.



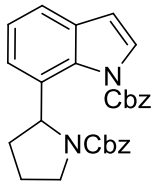
(±)-Benzyl 2-(4-((4-chlorophenyl)(methyl)carbamoyl)phenyl)pyrrolidine-1-carboxylate (2p)

Following the representative procedure, **2p** was obtained from *N*-(4-chlorophenyl)-*N*-methyl-4-vinylbenzamide (67.8 mg, 0.25 mmol, 2.0 equiv.) after 36 h, stirring at 105 °C. The product **2p** (33.6 mg, 60%) was isolated as colorless oil after flash column chromatography on silica gel (20 – 50% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.64 – 6.73 (m, 13H), 5.25 – 4.74 (m, 3H), 3.76 – 3.54 (m, 2H), 3.44 (s, 3H), 2.38 – 2.14 (m, 1H), 1.97 – 1.71 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 170.2, 154.9, 146.3, 145.6, 143.5, 136.5, 134.0, 133.8, 132.0, 129.3, 128.9, 128.4, 128.2, 128.0, 127.7, 127.2, 125.0, 66.6, 60.8, 47.6, 47.1, 38.5, 35.7, 34.5, 23.4, 22.9; IR neat film: 2922, 2851, 2649, 2286, 2324, 1703, 1647, 1576, 1492, 1413, 1392, 753 cm^{-1}; HRMS (EI) calcd for [$C_{26}H_{25}O_3N_2Cl_1$]: 448.1548; found 448.1558.



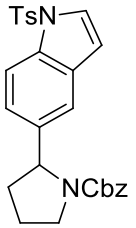
(±)-Benzyl 2-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (2q)

Following the representative procedure, **2q** was obtained from methyl-4-vinylbenzoate (40.1 mg, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 °C. The product **2q** (15.3 mg, 35%) was isolated as colorless oil after flash column chromatography on silica gel (10 - 11 % EtOAc/hexanes gradient). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.96 (d, *J* = 7.8 Hz, 2 H), 7.49 - 7.07 (m, 6 H), 6.89 (d, *J* = 6.8 Hz, 1 H), 5.24 - 4.89 (m, 3 H), 3.98 - 3.85 (m, 3 H), 3.76 - 3.58 (m, 2 H), 2.44 - 2.28 (m, 1 H), 1.99 - 1.78 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 166.9, 154.9, 148.9, 136.5, 129.8, 128.7, 128.5, 128.2, 128.0, 127.6, 127.4, 127.1, 125.5, 66.8, 61.3, 61.0, 52.1, 47.7, 47.2, 35.8, 23.0, 22.6; IR neat film: 2978, 1702 (broad, overlap), 1409, 1352, 1009, 771, 661 cm^{-1}; HRMS (EI) calcd for $[C_{20}H_{21}O_4N_1]$: 339.1465; found 339.1463.



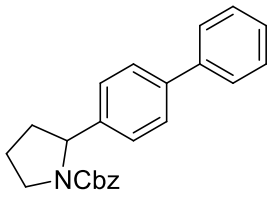
(±)-Benzyl 7-(1-(benzyloxycarbonyl)pyrrolidin-2-yl)-1H-indole-1-carboxylate (2r)

Following the representative procedure, **2r** was obtained from benzyl 7-vinyl-1H-indole-1-carboxylate (69.3 mg, 0.25 mmol, 2.0 equiv.) after 48 h, stirring at 105 °C. The product **2r** (44.4 mg, 78%) was isolated after flash column chromatography on silica gel (10-13 % EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.63 (d, *J* = 4.1 Hz, 1 H), 7.53 - 7.28 (m, 7 H), 7.26 - 6.99 (m, 4 H), 6.95 - 6.78 (m, 1 H), 6.65 - 6.50 (m, 1 H), 6.15 (d, *J* = 8.2 Hz, 0.3 H), 6.06 (dd, *J* = 2.6, 7.9 Hz, 0.6 H), 5.46 - 5.29 (m, 2 H), 5.23 - 5.07 (m, 1 H), 5.07 - 4.89 (m, 1 H), 3.80 - 3.53 (m, 2 H), 2.50 - 2.19 (m, 1 H), 2.05 - 1.69 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 155.1, 154.8, 151.0, 150.9, 137.2, 136.9, 135.1, 135.0, 132.4, 131.7, 130.9, 128.7, 128.5, 128.4, 128.1, 127.8, 127.2, 126.9, 123.7, 123.5, 122.6, 122.1, 119.8, 108.5, 68.9, 66.6, 66.3, 59.6, 59.0, 47.6, 47.2, 34.9, 34.2, 23.1, 22.6; IR neat film: 2928, 1748, 1696, 1410, 1312, 1203, 1023, 729, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{28}H_{27}O_4N_2]^+$: 455.1965; found 455.1967.



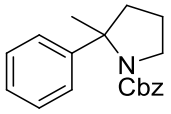
(±)-Benzyl 2-(1-tosyl-1H-indol-5-yl)pyrrolidine-1-carboxylate (2s)

Following the representative procedure, **2s** was obtained from 1-tosyl-5-vinyl-1H-indole (48.3 mg, 0.16 mmol, 1.3 equiv.) after 48 h, stirring at 105 °C. The product **2s** (37.3 mg, 63%) was isolated after flash column chromatography on silica gel (10-13 % EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 7.92 (d, *J* = 7.4 Hz, 1 H), 7.79 (d, *J* = 7.4 Hz, 2 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 7.45 - 6.99 (m, 7 H), 6.87 (br. s., 1 H), 6.69 (d, *J* = 5.8 Hz, 1 H), 6.58 (br. s., 1 H), 5.22 - 4.78 (m, 3 H), 3.80 - 3.53 (m, 2 H), 2.33 (d, *J* = 12.9 Hz, 4 H), 2.00 - 1.77 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) rotomeric mixture: δ 155.0, 144.9, 139.6, 138.7, 137.0, 136.5, 135.3, 133.8, 130.8, 129.9, 128.4, 128.2, 127.9, 127.3, 127.0, 126.8, 126.6, 122.5, 118.1, 117.9, 113.4, 109.0, 66.7, 66.5, 61.2, 61.0, 47.6, 47.2, 36.1, 35.0, 23.5, 22.9, 21.5; IR neat film: 2925, 1697, 1455, 1411, 1367, 1354, 1171, 1138, 1126, 1107, 1092811, 770, 676, 584 cm^{-1}; HRMS (EI) calcd for [$C_{27}H_{26}O_4N_2S_1$]: 474.1608; found 474.1602.



(±)-Benzyl 2-(biphenyl-4-yl)pyrrolidine-1-carboxylate (2t)

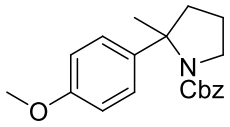
Following the representative procedure, **2t** was obtained from 4-vinylbiphenyl (90.0 mg, 0.25 mmol, 2.0 equiv.) after 24 h stirring at 105 °C. The product **2t** (27.2 mg, 61%) was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ: 7.70 - 7.04 (m, 13 H), 6.92 (d, J = 5.8 Hz, 1 H), 5.27 - 4.86 (m, 3 H), 3.83 - 3.56 (m, 2 H), 2.45 - 2.28 (m, 1 H), 2.11 - 1.81 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) rotomeric mixture δ: 155.0, 143.4, 142.6, 141.0, 140.9, 139.7, 137.0, 136.7, 128.7, 128.4, 128.1, 127.9, 127.5, 127.0, 125.9, 66.7, 66.5, 61.1, 60.9, 47.7, 47.2, 35.9, 34.8, 23.6, 23.0; IR neat thin film: 2958, 1701, 1410, 1351, 1107, 766, 698 cm^{-1}; HRMS (EI) calcd for [$C_{24}H_{23}N_1O_2$]: 357.1723; found 357.1728.



(±)-Benzyl 2-methyl-2-phenylpyrrolidine-1-carboxylate (3a)

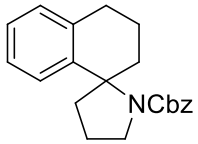
Following the representative procedure, **3a** was obtained from α-methyl styrene (29.6 mg, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **3a** (19.2 mg, 52%) was isolated as colorless oil after flash column chromatography on silica gel (10-11% EtOAc/hexanes gradient).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.72 - 7.06 (m, 8 H), 6.81 (d, J = 6.8 Hz, 1 H), 5.13 (ABq, $\Delta\nu_{AB}$ = 20 Hz, J_{AB} = 13 Hz, 1H), 4.96 (ABq, $\Delta\nu_{AB}$ = 30 Hz, J_{AB} = 13 Hz, 1H), 3.93 - 3.63 (m, 2 H), 2.22 - 2.00 (m, 2 H), 1.91 (s, 1 H), 1.89 - 1.68 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture δ: 154.9, 153.8, 147.6, 146.4, 137.3, 136.5, 128.4, 128.1, 128.0, 127.7, 127.3, 126.2, 126.1, 124.9, 66.4, 66.2, 66.1, 65.4, 49.3, 48.4, 45.9, 44.5, 25.9, 25.5, 22.0, 21.9; IR neat film: 2970, 1691, 1402, 1351, 761, 698 cm^{-1}; HRMS (EI) calcd for [$C_{19}H_{21}O_2N_1$]: 295.1567 found 295.1578.



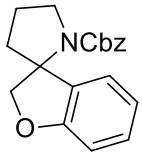
(±)-Benzyl 2-(4-methoxyphenyl)-2-methylpyrrolidine-1-carboxylate (3b)

Following the representative procedure, **3b** was obtained from 1-methoxy-4-(prop-1-en-2-yl)benzene (33.5 mg, 0.25 mmol, 2.00 equiv.) after 24 h, stirring at 105 ˚C. The product **3b** (27.6 mg, 68%) was isolated as colorless oil after flash column chromatography on silica gel (10-13% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.36 - 7.19 (m, 3 H), 7.15 - 7.00 (m, 3 H), 6.81 - 6.67 (m, 3 H), 5.02 (ABq, $\Delta\nu_{AB}$ = 14 Hz, J_{AB} = 13 Hz, 1H), 4.87 (ABq, $\Delta\nu_{AB}$ = 36 Hz, J_{AB} = 13 Hz, 1H), 3.78 - 3.59 (m, 5 H), 2.07 - 1.90 (m, 2 H), 1.84 - 1.59 (m, 5 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 158.0, 155.0, 153.7, 139.8, 138.6, 137.3, 136.6, 128.4, 128.0, 127.7, 127.4, 126.0, 113.5, 113.4, 66.4, 66.2, 65.7, 65.0, 55.2, 49.2, 48.4, 45.9, 44.5, 26.0, 25.6, 22.0, 21.9; IR neat film: 2968, 2933, 1698, 1608, 1512, 1406, 1352, 1248, 830, 738, 698 cm^{-1}; HRMS (EI) calcd for [$C_{20}H_{23}O_3N_1$]: 325.1672; found 325.1674.



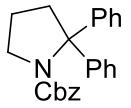
(±)-Benzyl 3,4-dihydro-2H-spiro[naphthalene-1,2'-pyrrolidine]-1'-carboxylate (3c)

Following the representative procedure, **3c** was obtained from 1-methylene-1,2,3,4-tetrahydronaphthalene (36.0 mg, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **3c** (24.9 mg, 62%) was isolated as colorless oil after flash column chromatography on silica gel (10-11%EtOAc/hexanes gradient). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.43 - 7.27 (m, 2 H), 7.24 - 6.95 (m, 6 H), 6.67 - 6.58 (m, 1 H), 5.03 (ABq, 0.8 H, $\Delta\nu_{AB}$ = 10 Hz, J_{AB} = 13 Hz), 4.81 (ABq, 1.2 H, $\Delta\nu_{AB}$ = 10 Hz, J_{AB} = 12 Hz), 3.94 - 3.64 (m, 2 H), 2.80 - 2.41 (m, 3 H), 2.35 - 2.16 (m, 2 H), 2.16 - 1.63 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 154.5, 153.1, 143.3, 142.4, 137.3, 137.1, 136.3, 135.5, 128.7, 128.5, 128.4, 128.0, 127.7, 127.4, 126.4, 126.1, 126.0, 126.0, 125.6, 125.1, 66.6, 66.1, 65.6, 65.3, 49.3, 48.6, 44.4, 43.3, 33.6, 32.6, 29.4, 23.0, 22.8, 22.4, 21.8; IR neat film: 2927, 1692, 1410, 1352, 1130, 754, 698 cm^{-1}; HRMS (EI) calcd for [$C_{19}H_{19}O_4N_1$]: 321.1723; found 321.1726.



Benzyl 2H-spiro[benzofuran-3,2'-pyrrolidine]-1'-carboxylate (3d)

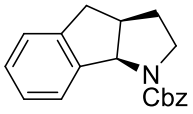
Following the representative procedure, **3d** was obtained from 3-methylene-2,3-dihydrobenzofuran (33.0 mg, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **3d** (22.1 mg, 57%) was isolated as colorless oil after flash column chromatography on silica gel (10-20% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.41 - 7.27 (m, 2 H), 7.25 - 7.05 (m, 3 H), 6.94 - 6.73 (m, 2 H), 6.70 (d, *J* = 7.8 Hz, 1 H), 5.11 (d, *J* = 12.5 Hz, 1 H), 5.01 - 4.75 (m, 2 H), 4.64 (d, *J* = 9.4 Hz, 1 H), 4.28 (d, *J* = 9.0 Hz, 1 H), 3.77 - 3.58 (m, 2 H), 2.32 - 2.19 (m, 2 H), 2.16 - 2.00 (m, 1 H), 1.98 - 1.79 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 160.0, 154.4, 141.2, 136.8, 136.6, 136.6, 136.0, 130.7, 129.9, 129.1, 128.4, 128.1, 127.5, 127.9, 127.5, 122.5, 122.3, 122.3, 120.7, 120.6, 109.9, 81.0, 80.0, 70.3, 69.9, 66.9, 66.5, 48.3, 47.5, 43.5, 42.0, 23.5, 23.0; IR neat film: 2967, 2886, 1699, 1604, 1480, 1406, 1352, 799, 750, 698 cm^{-1}; HRMS (EI) calcd for $[C_{19}H_{20}O_3N_1]$+: 310.1438; found 310.1434.



Benzyl 2,2-diphenylpyrrolidine-1-carboxylate (3e)

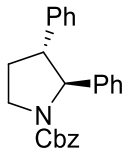
Following the representative procedure, **3e** was obtained from 1,1-dipheylethylene (45.0 mg, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **3e** (28.6 mg, 64%) was isolated as colorless oil after flash column chromatography on silica gel (10-11%EtOAc/hexanes gradient).

^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.97 - 6.89 (m, 13 H), 6.88 - 6.48 (m, 1 H), 5.24 - 4.92 (m, 0.8 H), 4.86 - 4.57 (m, 1.1 H), 4.00 - 3.71 (m, 2 H), 2.77 - 2.51 (m, 2 H), 1.94 - 1.67 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 155.2, 153.9, 143.5, 137.2, 136.1, 127.9, 127.7, 126.7, 73.0, 66.5, 49.2, 48.6, 47.9, 46.0, 22.7, 22.1; IR neat film: 2973, 1712, 1447, 1405, 1350, 1125, 756, 698 cm^{-1}; HRMS (EI) calcd for [$C_{24}H_{23}O_2N_1$]: 357.1723; found 357.1716.



(±)-Benzyl 2,3,3a,4-tetrahydroindeno[1,2-b]pyrrole-1(8bH)-carboxylate (3f)

Following the representative procedure, **3f** was obtained from 1H-indene (36.3 mg, 0.31 mmol, 2.5 equiv.) after 36 h, stirring at 120 ˚C in anhydrous 1,4-dioxane. The product **3f** (13.2 mg, 36%) was isolated as colorless oil after flash column chromatography on silica gel (0 -10% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.76 (d, *J* = 7.0 Hz, 0.5 H), 7.56 - 7.28 (m, 6 H), 7.25 - 7.03 (m, 2.5 H), 5.47 - 5.09 (m, 3 H), 3.69 - 3.48 (m, 1 H), 3.47 - 3.35 (m, 1 H), 3.19 - 3.05 (m, 2 H), 2.77 (d, *J* = 13.6 Hz, 1 H), 2.18 - 2.02 (m, 1 H), 1.72 - 1.59 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 155.6, 155.0, 143.4, 142.8, 141.8, 141.6, 137.0, 128.4, 128.2, 128.0, 127.8, 126.9, 126.2, 125.1, 124.9, 67.0, 66.9, 66.7, 66.3, 46.7, 46.4, 42.4, 41.3, 36.3, 36.1, 31.1, 30.3; IR neat film: 2928, 1699, 1412, 1112, 747, 698 cm^{-1}; HRMS (EI) calcd for [$C_{19}H_{19}O_2N_1$]: 293.1410; found 293.1406.

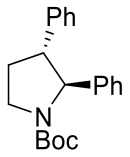


(±)-Benzyl 2,3-diphenylpyrrolidine-1-carboxylate (3g)

Following the representative procedure, **4b** was obtained from trans-stilbene (56.3 mg, 0.31 mmol, 2.5 equiv.) after 24 h stirring at 105 ˚C. The product **4b** (14.3 mg, 32%, > 20:1 dr)was isolated as colorless oil after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient).

Note: when cis-stilbene was used as starting materials, the same product and same diastereomer (11.2 mg, 25%) was formed.

By analogy to the **3h**, the Boc-functionalized analog (vide infra), the structure was assigned to have *trans*- configuration. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.56 - 6.99 (m, 14 H), 6.78 (d, J = 6.2 Hz, 1 H), 5.27 - 4.76 (m, 3 H), 4.10 - 3.88 (m, 1 H), 3.84 - 3.66 (m, 1 H), 3.34 - 3.21 (m, 1 H), 2.43 - 2.24 (m, 1 H), 2.18 - 2.01 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 154.9, 142.3, 142.5, 141.3, 136.5, 128.7, 128.4, 127.3, 126.9, 125.6, 68.3, 66.8, 55.4, 54.1, 47.4, 46.9, 32.5, 31.8; IR neat film: 2947, 1698, 1408, 1349, 1109, 754, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}O_2N_1]^+$: 358.1802 found 358.1809.



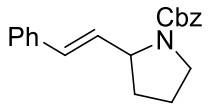
(±)-Tert-butyl 2,3-diphenylpyrrolidine-1-carboxylate (3h)

Following the general procedure, **3h** was obtained from trans-stilbene (12.9 mg, 0.312 mmol, 2.50 equiv.) and potassium (2-(tert-butoxycarbonylamino)ethyl) trifluoroborate salt after 36 h stirring at 105 ˚C. The product **3h** (12.9 mg, 32%, > 20:1 dr) was isolated as colorless oil was isolated after flash column chromatography on silica gel (10 – 11% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.43 - 6.97 (m, 10 H), 4.94 (brs, 0.2 H), 4.65 (brs, 0.7 H), 4.04 - 3.78 (m, 1 H), 3.71 (d, *J* = 6.6 Hz, 1 H), 3.24 (d, *J* = 6.6 Hz, 1 H), 2.35 - 2.21 (m, 1 H), 2.21 - 1.98 (m, 1 H), 1.46 (d, *J* = 5.8 Hz, 2 H), 1.23 - 1.02 (m, 7 H); ^{1}H NMR (400 MHz, $CDCl_3$, 50 ˚C): δ 7.39 - 6.97 (m, 10 H), 5.01 - 4.54 (m, 1 H), 4.05 - 3.83 (m, 1 H), 3.79 - 3.62 (m, 1 H), 3.32 - 3.16 (m, 1 H), 2.35 - 2.21 (m, 1 H), 2.11 (d, *J* = 8.6 Hz, 1 H), 1.56 - 0.94 (m, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 154.4, 144.0, 141.1, 128.6, 128.1, 127.4, 126.9, 126.7, 125.8, 79.4, 68.8, 67.5, 55.5, 54.4, 46.9, 32.0, 28.1IR neat film: 2974, 1693, 1393, 1166, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{25}O_2N_1\,N\,a_1]^+$: 346.1788; found 346.1782.

Determination of configuration of (±)-(2S,3R)-benzyl 2,3-diphenylpyrrolidine-1-carboxylate and (±)-(2S,3R)-tert-butyl 2,3-diphenylpyrrolidine-1-carboxylate (3h)

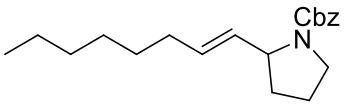
Boc-pyrrolidine **3h** (16 mg, 0.049 mmol) was treated with CF_3CO_2H (1 mL) in anhydrous DCM (2 mL) at 0 ˚C and stirred overnight. The product 2,3-diphenylpyrrolidine (8 mg, 73%) was isolated as yellow oil after flash column chromatography on silica, 50% EtOAc/hexanes. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.49 - 6.92 (m, 10 H), 4.19 (d, J = 9.4 Hz, 1 H), 3.48 - 3.16 (m, 3 H), 3.00 (brs, 1 H), 2.53 - 2.36 (m, 1 H), 2.24 - 2.02 (m, 1 H); HRMS (EI) calcd for $[C_{16}H_{17}N_1]$: 223.1356; found 223.1360.

The ^{1}H NMR data for the *cis*-2,3-diphenylpyrrolidine has been previously reported by Szymoniak. Our spectrum was similar but not identical, indicating we had formed the *trans*-diastereomer. The coupling constant for the doublet signal of the H alpha to N on the tertiary amine carbon (at 4.19 ppm) was also larger in our diastereomer than in Szymoniak's, as would be expected for the respective *cis* and *trans* diastereomers.[17]



(±)-(E)-benzyl 2-styrylpyrrolidine-1-carboxylate (4a)

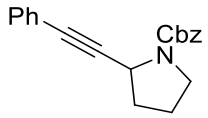
Following the representative procedure, **4a** was obtained from (E)-buta-1,3-dienylbenzene (65.1 mg, 0.50 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **4a** (52.2 mg, 68%) was isolated as colorless oil after flash column chromatography on silica gel (0 - 10% EtOAc/hexanes gradient). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.58 - 7.02 (m, 9 H), 6.62 – 6.01 (m, 1H), 5.36 – 5.01 (m, 1 H), 4.68 - 4.42 (m, 1 H), 3.69 – 3.44 (m, 2H), 2.28 - 1.68 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 155.0, 154.8, 136.7, 130.1, 129.8, 128.4, 127.8, 127.3, 126.3, 66.7, 58.9, 46.7, 46.3, 32.5, 31.5, 23.6, 22.9; IR neat film: 2962, 1698, 1449, 1411, 1353, 1093, 1028, 965, 750, 695 cm^{-1}; HRMS (EI) calcd for [$C_{20}H_{21}O_4N_1$]: 307.1567 found 307.1566.



(±)- (E)-benzyl 2-(oct-1-enyl)pyrrolidine-1-carboxylate (4b)

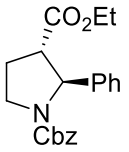
Following the representative procedure, **4b** was obtained from (E)-deca-1,3-diene (69 mg, 0.50 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **4b** (49.0 mg, 62%) was isolated as colorless oil after flash column chromatography on silica gel (0-10% EtOAc/hexanes gradient).

^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.42 - 7.26 (m, 5 H), 5.57 - 5.26 (m, 2 H), 5.19 - 5.05 (m, 2 H), 4.45 - 4.23 (m, 1 H), 3.55 - 3.34 (m, 2 H), 2.04 - 1.76 (m, 4 H), 1.76 - 1.62 (m, 2 H), 1.43 - 1.13 (m, 8 H), 0.96 - 0.79 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 155.1, 150.3, 137.2, 136.1, 130.9, 130.0, 129.5, 128.3, 127.7, 126.5, 123.1, 66.5, 58.6, 46.6, 32.5, 32.1, 31.7, 29.6, 29.2, 28.8, 27.4, 23.5, 22.6, 14.1; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 154.7, 150.3, 146.0, 137.1, 136.1, 130.9, 130.0, 129.5, 128.3, 127.7, 126.5, 123.1, 66.5, 58.8, 58.6, 46.6, 46.3, 32.1, 31.7, 29.2, 28.8, 23.5, 22.6, 14.1; IR neat film: 2956, 2926, 2856, 1703, 1411, 1353, 1114, 1094, 769, 735, 697 cm^{-1}; HRMS (EI) calcd for [$C_{20}H_{30}O_2N_1$]: 316.2271; found 316.2275.



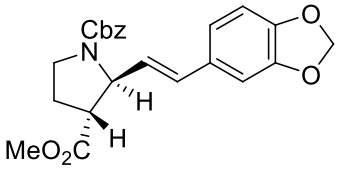
(±)-Benzyl 2-(phenylethynyl)pyrrolidine-1-carboxylate (5)

Following the representative procedure, **5** was obtained from but-3-en-1-ynylbenzene (32.0 mg, 0.25 mmol, 2.0 equiv.) after 24 h, stirring at 105 ˚C. The product **5** (13.3 mg, 35%) was isolated as yellow oil after flash column chromatography on silica gel (0-10% EtOAc/hexanes gradient). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.53 - 7.12 (m, 10 H), 5.44 - 5.02 (m, 2 H), 4.93 - 4.68 (m, 1 H), 3.74 - 3.29 (m, 2 H), 2.26 - 2.03 (m, 3 H), 2.03 - 1.90 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 154.5, 136.9, 131.7, 128.4, 128.1, 122.9, 89.4, 82.2, 66.8, 49.2, 48.7, 46.2, 45.8, 34.0, 33.3, 23.7; IR neat film: 3062, 2972, 2929, 2836, 1718, 1692, 1651, 1513, 1393, 1246, 1165, 1113, 1036, 828, 713 cm^{-1}; HRMS (EI) calcd for [$C_{20}H_{19}N_1O_2$]: 305.1410; found; 305.1406.

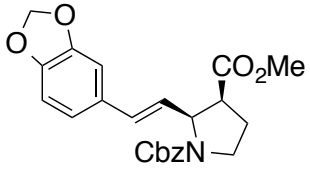


(±)-1-benzyl 3-ethyl 2-phenylpyrrolidine-1,3-dicarboxylate (6)

Following the representative procedure, **6** was obtained from but-3-en-1-ynylbenzene (55 mg, 0.31 mmol, 2.5 equiv.) after 24 h, stirring at 105 ˚C. The product **6** (14.6 mg, 33%, > 20:1 dr) was isolated as colorless oil after flash column chromatography on silica gel (0-10% EtOAc/hexanes gradient). By analogy to the **3h** and **7**, the structure is assigned to have *trans* configuration. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.56 – 7.07 (m, 8H), 6.97 – 6.75 (m, 1H), 5.44 – 4.82 (m, 3H), 4.18 (q, J = 7.1 Hz, 1H), 3.98 – 3.61 (m, 2H), 3.09 – 2.87 (m, 1H), 2.33 – 2.08 (m, 2H), 1.26 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 172.6, 154.7, 142.8, 142.1, 136.8, 136.5, 128.6, 128.1, 127.9, 127.4, 127.2, 125.5, 66.7, 64.0, 63.5, 61.1, 53.3, 52.1, 46.9, 46.4, 26.8, 14.1; IR neat film: 2981, 1732, 1705, 1410, 1352, 1179, 1113, 769, 699 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{24}O_4N_1]^+$: 354.1700; found 354.1709.



(7)-*trans*



(7)-*cis*

(E)- and (Z)-benzyl 3-acetyl-2-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)pyrrolidine-1-carboxylate (7)

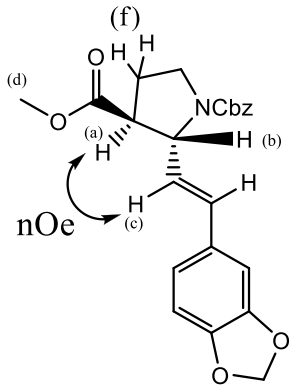
Following the representative procedure, **7**-*trans* and **7**-*cis* were obtained from (2E,4E)-methyl 5-(benzo[d][1,3]dioxol-5-yl)penta-2,4-dienoate (67.5 mg, 0.3125 mmol, 2.5 equiv.) after 24 h, stirring at 105 °C. The product **7**-*trans* and **7**-*cis* (30.7 mg, 60%) (dr = 5:1) were obtained as a mixture from by flash column chromatography on silica gel (0-20% EtOAc/hexanes gradient). The two diastereomers were further separated by HPLC (85:15 to 75:25 hexanes:EtOAc gradient).

(**7**)-*trans*: HPLC (85:15 to 75:25 hexanes:EtOAc gradient, Varian Dynamax 250x21.4 mm (LxID) microsorb 100-5 Si), Rt: 56 mins. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.46 - 7.09 (m, 4 H), 6.93 - 6.62 (m, 3 H), 6.53 - 6.19 (m, 1 H), 6.05 - 5.80 (m, 3 H), 5.33 - 4.92 (m, 2 H), 4.87 - 4.68 (m, 1 H), 3.79 - 3.62 (m, 4 H), 3.62 - 3.45 (m, 1 H), 3.00 - 2.82 (m, 1 H), 2.30 - 2.06 (m, 2 H); ^{1}H NMR (500 MHz, $CDCl_3$, 60 ˚C) rotomeric mixture: δ 7.42 - 7.18 (m, 5 H), 6.84 (br. s., 1 H), 6.73 (s, 2 H), 6.39 (d, *J* = 15.6 Hz, 1 H), 5.99 - 5.87 (m, 3 H), 5.26 - 4.99 (m, 2 H), 4.81 (br. s., 1 H), 3.81 - 3.65 (m, 4 H), 3.65 - 3.44 (m, 1 H), 3.00 - 2.84 (m, 1 H), 2.29 - 2.07 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 173.1, 147.9, 147.3, 139.4, 136.7, 130.8, 130.6, 128.4, 127.8, 126.8, 121.3, 108.2, 105.8, 101.0, 66.9, 61.6, 52.2, 50.1, 45.9, 26.6; (**7**)-*cis*: HPLC (85:15 to 75:25 hexanes:EtOAc gradient, Varian Dynamax 250x21.4 mm (LxID) microsorb 100-5 Si), Rt: 60 mins. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 7.45 – 7.14 (m, 5 H), 6.90 - 6.63 (m, 3 H), 6.46 (d, *J* = 16.1 Hz, 0.4H), 6.30 (d, *J* = 15.6 Hz, 0.6 H), 5.98 - 5.90 (m, 2 H), 5.81 (dd, *J* =

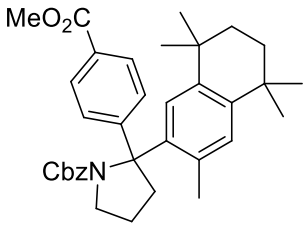
14.9, 6.6 Hz, 1 H), 5.21 - 5.00 (m, 2 H), 4.86 - 4.70 (m, 1 H), 3.75 - 3.66 (m, 1 H), 3.63 (s, 3 H), 3.48 (d, *J* = 7.8 Hz, 1 H), 3.23 (brs, 1 H), 2.35 (d, *J* = 9.3 Hz, 1 H), 2.11 (dt, *J* = 12.8, 6.5 Hz, 1 H); ^{1}H NMR (500 MHz, $CDCl_3$, 60 ˚C) rotomeric mixture: δ 7.42 - 7.25 (m, 6 H), 6.81 (brs, 1 H), 6.72 (brs, 2 H), 6.36 (brs, 1 H), 5.93 (s, 2 H), 5.82 (dd, *J* = 15.9, 7.6 Hz, 1 H), 5.24 - 5.01 (m, 2 H), 4.79 (brs, 1 H), 3.75 - 3.67 (m, 1 H), 3.64 (s, 2 H), 3.56 - 3.43 (m, 1 H), 3.29 - 3.15 (m, 1 H), 2.45 - 2.26 (m, 1 H), 2.11 (dt, *J* = 12.3, 6.3 Hz, 1 H); IR neat film: 2952, 1732, 1696, 1629, 1491, 1091, 812, 759 cm^{-1}; HRMS (EI) calcd for [$C_{23}H_{23}O_6N_1$]: 409.1520; found 409.1520.

Note: nOe experiment was done to determine relative configuration. (see below)

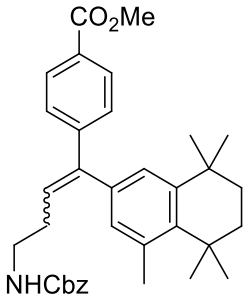
Determination of absolute configuration of compound (7)



The configuration of the major product **(7)** was done by using nOe analysis. Upon the irradiation of proton H_a (2.91 ppm), the nOe signal between H_a and $H_{c\ at}$ 5.89-5.93 ppm was observed. This is a clear indication that the proton H_a and the proton H_c of the alkene must be on the same side in order for this nOe signal to occur. From this analysis, it can be concluded that the configuration of major product (7) is *trans*.



Benzyl 2-(4-(methoxycarbonyl)phenyl)-2-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)pyrrolidine-1-carboxylate (8)



(E/Z)-Methyl 4-(4-(benzyloxycarbonylamino)-1-(4,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)but-1-enyl)benzoate (9)

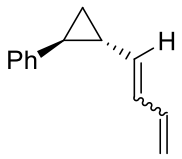
Following the general procedure, **8** was obtained from bexarotene methyl ester (90.5 mg, 0.25 mmol, 2.0 equiv.) after 36 h, stirring at 105 °C. The product **8** (24.3 mg, 36%) was isolated as colorless oil after flash column chromatography on silica gel (0 – 25% EtOAc/hexanes gradient). Also 1:1 E/Z mixture of Heck products **9** were also obtained (11.1 mg, 16%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 8.15 - 7.62 (m, 2 H), 7.59 - 6.84 (m, 8 H), 6.61 (d, *J* = 5.9 Hz, 1 H), 5.25 - 5.01 (m, 0.5 H),, 4.94 - 4.48 (m, 1.5 H), 4.00 - 3.66 (m, 5 H), 2.89 - 2.36 (m, 2 H), 2.08 - 1.86 (m, 4 H), 1.85 - 1.57 (m, 6 H), 1.36 - 1.00 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 166.9, 155.1, 153.5, 149.6, 148.9, 143.4, 141.5, 137.2, 136.8, 136.4, 135.8, 131.7, 130.2, 128.6, 128.5, 128.3, 127.9, 127.5, 125.8, 125.4, 77.4, 76.6, 72.5, 66.6, 51.9, 49.1, 48.6, 44.2, 42.8, 35.2, 35.1,

33.8, 33.7, 31.9, 31.6, 23.2, 22.7, 22.3; IR neat film: 2980, 2970, 2927, 1723, 1660, 1388, 1278, 1260, 1109, 799, 699 cm^{-1}; HRMS (EI) calcd for $[C_{35}H_{41}O_4N_1]$: 539.3030 found 539.3036.

Alkene 9 (E and Z mixture, 1:1, 11.1 mg, 16%):

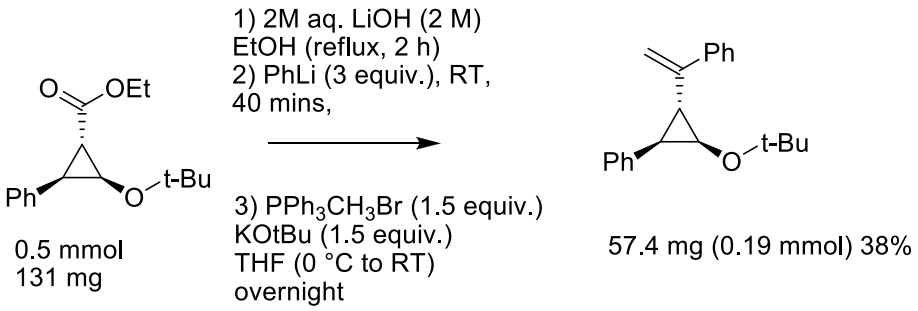
^1H NMR (500MHz, $CDCl_3$, 25 ˚C) δ: 8.04 - 7.84 (m, 4 H), 7.41 - 7.18 (m, 14 H), 7.09 (d, *J* = 8.3 Hz, 2 H), 6.97 (d, *J* = 19.0 Hz, 2 H), 6.26 (t, *J* = 7.3 Hz, 1 H), 5.72 (t, *J* = 7.3 Hz, 1 H), 5.20 - 4.99 (m, 4 H), 4.78 - 4.51 (m, 2 H), 3.90 (d, *J* = 7.8 Hz, 6 H), 3.44 - 3.21 (m, 4 H), 2.49 (q, *J* = 7.2 Hz, 2 H), 2.27 - 2.09 (m, 2 H), 2.02 - 1.84 (m, 6 H), 1.69 (d, *J* = 8.8 Hz, 8 H), 1.31 (s, 6 H), 1.27 (s, 12 H), 1.23 (br. s., 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) rotomeric mixture: δ 167.0, 156.3, 145.7, 144.1, 143.2, 142.4, 135.1, 132.9, 129.6, 128.5, 128.1, 127.9, 126.2, 66.7, 52.0, 40.6, 35.2, 34.0, 33.9, 31.9, 30.7, 29.7, 19.3; IR neat film: 3341, 2957, 2924, 1722 (overlap), 1605, 1278, 1110, 772, 698 cm^{-1}; HRMS (ESI) calcd for M+Na, $[C_{35}H_{41}O_4NNa]^+$: 562.2928 found 562.2930.

Radical Clock Mechanism Probes



(±)-((1S,2R)-2-(buta-1,3-dienyl)cyclopropyl)benzene

To the suspension of allyltriphenylphosphonium bromide (498 mg, 1.30 mmol, 1.3 equiv) was suspended in 5 mL of anhydrous THF at to 0 °C was added solution of 1.6 M nBuLi in THF (0.81 mL) dropwise. The red mixture was allowed to warm to room temperature and was stirred for 30 minutes. Then, a solution of (±)-(1S,2S)-2-phenylcyclopropanecarbaldehyde[18] (146 mg, 1.00 mmol, 1.0 equiv) in 1.0 mL of anhydrous THF was added dropwise at 0 °C. When the addition was completed, the ice-bath was removed and the reaction was allowed to warm up to room temperature and stir overnight. Once all the aldehyde was consumed, the reaction was quenched with 10 mL of brine. The aq. layer was extracted with Et_2O (3x15 mL) and dried over Na_2SO_4 then concentrated to give a crude oil. The diene was purified by flash chromatography on silica gel (10:1 hexanes:Et_2O eluent). The product, a mixture of E and Z isomers (1:1), was obtained as pale yellow oil (54.6 mg, 32%). The product was ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 - 7.35 (m, 10 H), 6.75 (dt, *J*=16.9, 10.7 Hz, 1 H), 6.31 (dt, *J*=17.2, 10.6 Hz, 1 H), 6.16 (dd, *J*=14.7, 10.7 Hz, 1 H), 6.01 (t, *J*=10.9 Hz, 1 H), 5.43 (dd, *J*=14.8, 8.6 Hz, 1 H), 5.20 (d, *J*=17.2 Hz, 1 H), 5.13-4.91 (m, 3 H), 2.06-1.88 (m, 2 H), 1.76-1.63 (m, 1 H), 1.36-1.21 (m, 2 H), 1.17-1.04 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 137.0, 136.8, 134.9, 132.5, 129.3, 128.3, 128.2, 125.7, 125.7, 125.6, 116.9, 114.6, 26.8, 25.8, 25.7, 23.3, 17.5, 17.1; IR (thin film): 3027, 1723, 1697, 1644, 968, 748, 696; HRMS (EI) calcd for $[C_{13}H_{14}]^+$ 170.1090; found 170.1091.

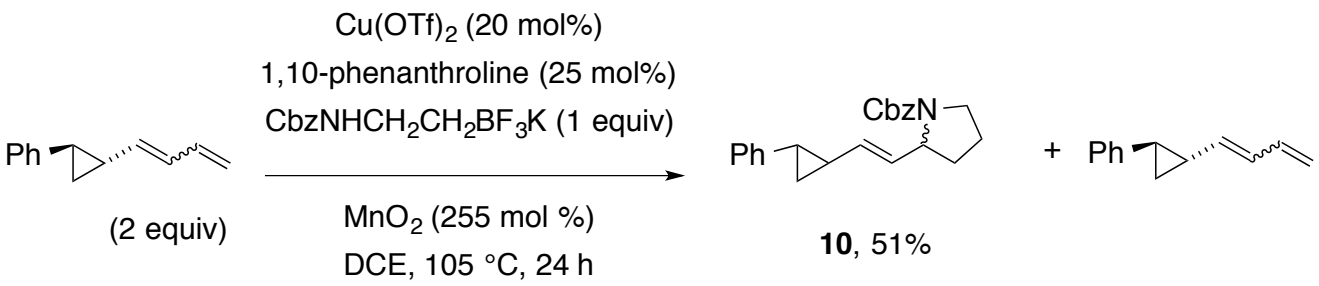


(±)-((1*R*,2*S*,3*R*)-2-(*tert*-butoxy)-3-(1-phenylvinyl)cyclopropyl)benzene

To the solution of (±)-(1S,2S,3R)-ethyl 2-tert-butoxy-3-phenylcyclopropanecarboxylate[19] (131 mg, 0.50 mmol) in absolute ethanol (2 mL) was added aq. solution of LiOH (2 M) (0.5 mL, 1 mmol, 2 equiv). After 2 hours of reflux, the volatile component was evaporated using rotovap and the liquid phase was extracted with EtOAc multiple times. The combined organic phase was dried over Na_2SO_4 and concentrated and placed under high vacuum to give a white solid that was used for the next step without purification. (Note: the compound seems to be acid sensitive so silica gel column chromatography was avoided.) After placing the solid under high vacuum for 4 hours, the white solid was dissolved in anhydrous Et_2O (2 mL) followed by the dropwise addition of PhLi (0.8 mL, 1.5 mmol of a 1.8 M in THF, 3 equiv). The red solution was allowed to stir at room temperature for another 20 minutes and the reaction was then quenched with 2.5 mL of a 0.4 M aqueous NH_4Cl solution, whereupon the mixture turned yellow. The mixture was extracted with Et_2O. The combined organic phase was washed with brine and then dried over Na_2SO_4 and concentrated in vacuo to give a yellow oil which was used for the subsequent Wittig reaction step without further purification.

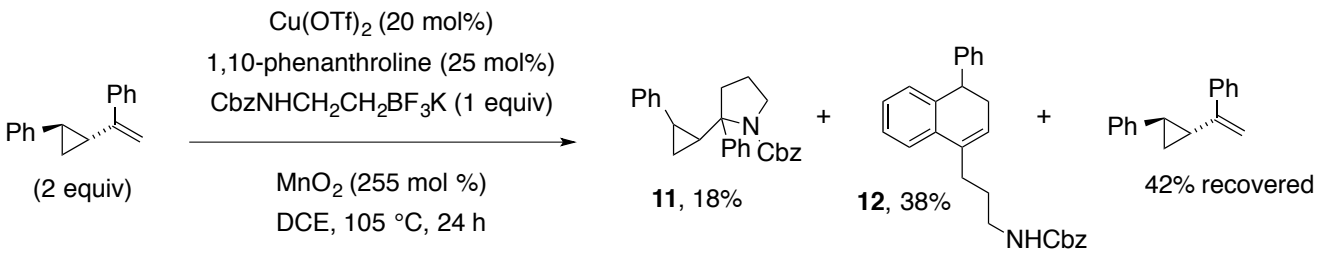
To a suspension of methyltriphenylphosphonium bromide (267 mg, 0.75 mmol, 1.5 equiv) in 2.5 mL of anhydrous THF at to 0 °C was added a solution of potassium *tert*-butoxide (84 mg, 0.75 mmol, 1.5 equiv) in THF (2.5 mL) dropwise. The yellow mixture was allowed to warm to room

temperature and was stirred for 30 minutes. Then, a solution of the above-described crude ketone in 1.0 mL of anhydrous THF was added dropwise at 0 °C. When the addition was complete, the reaction was allowed to warm to room temperature and was stirred overnight. Once all the starting material was consumed, the reaction was quenched with 10 mL of brine. The aq. layer was extracted with Et_2O (15 mL x 3) and dried over Na_2SO_4 then concentrated to give a crude oil. The alkene was purified by flash chromatography on silica gel (10:1 hexanes:Et_2O) to give a yellow oil (57.4 mg, 0.19 mmol, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2 H), 7.36 - 7.27 (m, 7 H), 7.20 (dd, *J* = 8.4, 4.1 Hz, 1 H), 5.39 (s, 1 H), 5.05 (s, 1 H), 3.66 (dd, *J* = 6.1, 4.1 Hz, 1 H), 2.28 - 2.21 (m, 1 H), 2.14 (t, *J* = 6.6 Hz, 1 H), 1.12 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 140.6, 138.4, 133.8, 133.6, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 126.8, 126.4, 126.0, 125.4, 109.6, 74.9, 59.2, 32.9, 31.6, 27.8; IR (thin film): 3059, 3025, 2974, 1189, 720, 696; HRMS (EI) calcd for $[C_{21}H_{24}O]^+$ 292.1822; found 292.1821.



Benzyl 2-(2-(2-phenylcyclopropyl)vinyl)pyrrolidine-1-carboxylate (10)

Following the general procedure, pyrrolidines **10** were obtained from (±)-((1*R*,2*S*)-2-(buta-1,3-dien-1-yl)cyclopropyl)benzene (85.2 mg, 0.5 mmol, 2.0 equiv), and potassium benzyl *N*-[2-(trifluoroboranyl)ethyl]carbamate (**1a**) (71.2 mg, 0.25 mmol, 1.0 equiv) after 24 h stirring at 105 ˚C. Pyrrolidines **10** (47.2 mg, 51%), a colorless oil, were obtained as a diastereomeric and rotomer mixture after flash column chromatography on silica gel (10 – 20 % EtOAc/hexanes gradient). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 - 7.57 (m, 10 H), 5.36 - 5.61 (m, 1 H), 4.98 - 5.36 (m, 3 H), 4.22 - 4.52 (m, 1H), 3.12 - 3.54 (m, 2 H), 1.49 - 2.12 (m, 6 H), 0.82 - 1.31 (m, 2 H); ^{13}C NMR (75MHz, $CDCl_3$) δ 155.0, 142.6, 142.4, 137.1, 132.9, 132.8, 128.9, 128.4, 128.3, 127.8, 125.6, 66.6, 58.5, 46.6, 46.2, 32.6, 31.7, 26.1, 25.0, 23.6, 22.8, 16.8; IR (thin film): 2970, 2877, 1698, 1411, 748, 697; HRMS (ESI) calcd for $[C_{23}H_{26}O_2N_1]^+$: 348.1958 found 348.1971.



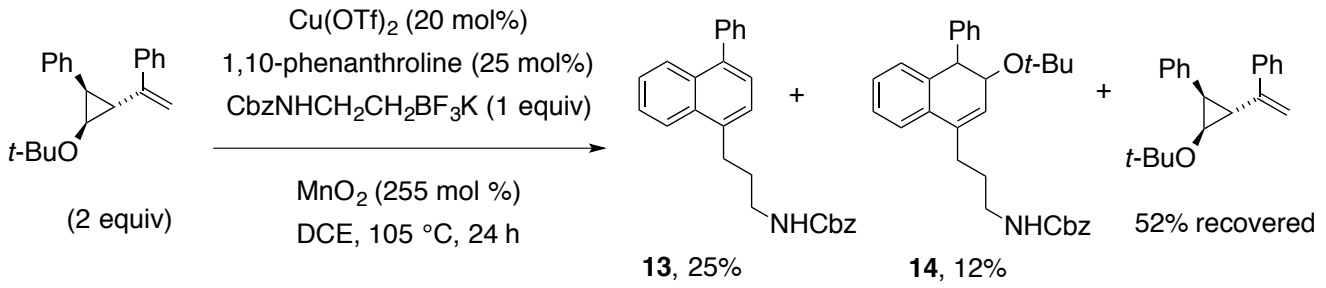
Following the general procedure, a mixture of pyrrolidines **11** and dihydronaphthalene **12** were obtained from (±)-(1-((1S,2S)-2-phenylcyclopropyl)vinyl)benzene[20] (110 mg, 0.5 mmol, 2.0 equiv) and potassium benzyl *N*-[2-(trifluoroboranyl)ethyl]carbamate (**1a**) (71.2 mg, 0.25 mmol, 1.0 equiv) after 24 h stirring at 105 ˚C. Following flash chromatography on silica gel (10-20 EtOAc/hexanes gradient), pyrrolidines **11** (17.9 mg, 18%), a colorless oil, were obtained as a mixture of diastereomers and rotamers and dihydronaphthalene **12** (37.5 mg, 38%) was isolated as colorless oil. The regiochemistry of dihydronaphthalene **12** is supported by COSY.

Benzyl 2-phenyl-2-(2-phenylcyclopropyl)pyrrolidine-1-carboxylate (11)

^{1}H NMR (400MHz, $CDCl_3$) δ: 7.49 - 6.65 (m, 15 H), 5.32 - 4.38 (m, 2 H), 4.00-3.50 (m, 2 H), 2.59 - 1.90 (m, 2 H), 1.90 - 1.68 (m, 4 H), 1.38 - 0.62 (m, 2.0 H); ^{13}C NMR (101MHz, $CDCl_3$) δ: 155.0, 153.8, 147.5, 146.7, 142.2, 137.3, 136.6, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 127.3, 126.8, 126.5, 126.4, 126.0, 125.9, 125.7, 125.5, 125.4, 125.3, 69.7, 69.2, 66.6, 66.5, 66.3, 66.2, 49.5, 48.8, 38.9, 38.0, 37.8, 36.7, 30.8, 30.4, 29.2, 23.0, 21.6, 21.3, 20.9, 18.5, 14.9, 11.5, 11.4; IR (thin film): 3028, 2952, 2877, 1687, 1400, 1351, 755, 697; HRMS (ESI) calcd for $[C_{27}H_{28}O_2N_1]^+$: 398.2115 found 398.2113.

Benzyl (3-(4-phenyl-3,4-dihydronaphthalen-1-yl)propyl)carbamate (12)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 - 7.02 (m, 13 H), 6.85 (d, *J* = 7.6 Hz, 1 H), 5.89 - 5.74 (m, 1 H), 5.10 (brs, 2 H), 4.75 (brs, 1 H), 4.05 (t, *J* = 8.2 Hz, 1 H), 3.32 - 3.11 (m, 2 H), 2.69 - 2.44 (m, 4 H), 1.77 (d, *J* = 5.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 144.1, 139.0, 136.6, 135.6, 134.4, 128.5, 128.4, 128.3, 128.1, 127.1, 126.7, 126.4, 123.9, 122.7, 66.6, 44.1, 40.8, 31.4, 29.9, 28.5; IR (thin film): 3332, 3028, 2937, 1698, 1518, 1453, 1248, 761, 699; HRMS (ESI) calcd for $[C_{27}H_{28}O_2N_1]^+$: 398.2115 found 398.2114.



Following the general procedure, naphthalene **13** and dihydronaphthalene **14** were obtained from (±)-((1*R*,2*S*,3*R*)-2-(*tert*-butoxy)-3-(1-phenylvinyl)cyclopropyl)benzene (72.4 mg, 0.25 mmol, 2.0 equiv), and potassium benzyl *N*-[2-(trifluoroboranidyl)ethyl]carbamate (**1a**) (35.6 mg, 0.13 mmol, 1.0 equiv) after 24 h stirring at 105 ˚C. A mixture of **13** and **14** (24.4 mg) were obtained following flash chromatography. The mixture was separated using HPLC (85% hexanes: 15% EtOAc to 80% hexanes: 20% EtOAc). Naphthalene **13**, retention time = 28 minutes, 12.3 mg (25%) and dihydronaphthalene **14** retention time = 31 minutes, 7.3 mg (12%), were obtained. The 4-phenylnaphthalene isomer **13** was assigned in preference to its 3-phenylnaphthalene isomer based on NMR spectra correlation with literature compounds 1-methyl-4-phenylnaphthalene[21] and 1-methyl-3-phenylnaphthalene.[22] The regiochemistry of the dihydronaphthalene product **14** was assigned by COSY.

Benzyl (3-(4-phenylnaphthalen-1-yl)propyl)carbamate (13)

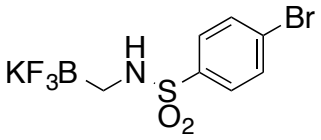
^{1}H NMR (300MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1 H), 7.92 (d, *J* = 8.2 Hz, 1 H), 7.60 - 7.28 (m, 13 H), 5.12 (s, 2 H), 4.81 (br. s., 1 H), 3.45 - 3.25 (m, 2 H), 3.16 (t, *J* = 7.3 Hz, 2 H), 2.12 - 1.95 (m, 2 H); ^{13}C NMR (75MHz, $CDCl_3$) δ : 156.4, 140.9, 139.0, 136.9, 136.6, 132.0, 131.9, 130.1, 128.5, 128.2, 128.1, 127.1, 127.0, 126.6, 125.7, 125.6, 123.8, 66.7, 41.0, 30.8, 30.3; IR (thin film): 3417, 3332, 3061, 3032, 2870, 2936, 1698, 1515, 1243, 769, 701; HRMS (ESI) calcd for M+Na, [$C_{27}H_{25}O_2NN$ a]: 418.1778; found 418.1780.

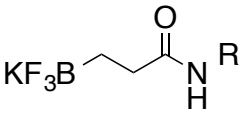
Benzyl (3-(3-(*tert*-butoxy)-4-phenyl-3,4-dihydronaphthalen-1-yl)propyl)carbamate (14)

^{1}H NMR (300MHz, $CDCl_3$) δ 7.60 - 7.30 (m, 8 H), 7.24 - 7.06 (m, 5 H), 7.02 - 6.88 (m, 1 H), 5.79 - 5.69 (m, 1 H), 5.09 (br. s., 2 H), 4.91 - 4.78 (m, 1 H), 4.35 - 4.28 (m, 1 H), 4.15 (d, *J* = 7.6 Hz, 1 H), 3.36 - 3.24 (m, 2 H), 2.58 - 2.48 (m, 2 H), 1.86 - 1.73 (m, 2 H), 1.04 (s, 9 H); IR (thin film): 3335, 3029, 2927, 1719, 1131, 756, 698; HRMS (ESI) calcd for M+Na, [$C_{31}H_{35}O_3NNa$]: 492.2509; found 492.2500. The ^{13}C NMR spectra was not obtained. Upon sitting in $CDCl_3$ (overnight NMR), the sample decomposed to give naphthalene **13**.

Attempted Coupling Reactions with Other Alkyltrifluoroborates:

The alpha-, beta- and gamma-amino alkyltrifluoroborates whose structures are given below, purchased from commercial vendors or synthesized as previously reported, did not provide nitrogen heterocycle products when submitted to coupling with 4-methoxystyrene under the optimized coupling conditions.





R = H, R = Ph, R = Bn

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