Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Application of Iridium Catalized Allylic Substitution Reactions in the Synthesis of Branched Tryptamines and Homologues via Tandem Hydroformylation/Fischer Indole Synthesis

Bojan P. Bondzić, Andreas Farwick, Jens Liebich and Peter Eilbracht*
Technische Universität Dortmund, Fachbereich Chemie, Organische Chemie I, Otto-Hahn-Str. 6, 44227 Dortmund. E-mail: peter.eilbracht@udo.edu; Fax: 49-231-7555363; Tel: 49-231-7553858

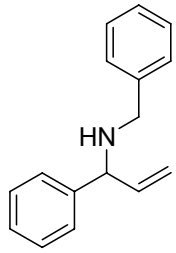
General procedures. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker AdvanceDRX400 spectrometer or a Bruker Advance DRX 500 spectrometer using $CDCl_3$ as solvent with $CHCl_3$ as internal standard. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in Hertz (Hz).The proton spectra are reported as follows δ/ppm (multiplicity, number of protons, coupling constant *J*/Hz). Two dimensional spectra (COSY, HSQC, HMBC) were used where appropriate to aid the assignments in ^{1}H and ^{13}C spectra. High resolution mass analyses were performed on a Jeol JMS-SX 102A. IR spectra were measured on a Nicolet Impact 400D FT-IR spectrometer. IR spectra were recorded as films on NACl or KBr plates or for solids pressed with KBr. The peak intensities are defined as very strong (vs), strong (s), middle (m) or weak (w). Optical rotations were measured on a Perkin-Elmer 341 polarimeter in a 10 cm cell in the stated solvent ; $[\alpha]_D$ values are given in 10^{-1}deg.cm^{2}g^{-1} (concentration *c* given as g/100 mL). Enantiomeric excesses were determined by analytical HPLC, Hewlet-Packard 1050 series chromatograph using a CHIRALCELL OD-H (250x4.6 mm), CHIRALCELL OJ-H (250x4.6 mm) and CHIRALPAK AD (250x4.6 mm) columns as noted. Column chromatography was carried out on 70–230 mesh silica gel (Macherey–Nagel; silicagel 60) using Cyclohexane/EA, Cyclohexane/MTBE or CH_2Cl_2/MeOH as eluents.

All Ir catalyzed reactions were conducted using standard Schlenk techniques. THF was distilled from sodium-benzophenone ketyl under nitrogen, CH_2Cl_2 was distilled from CaH_2 under nitrogen. All other solvents were purchased and used as received. $[Ir(cod)Cl]_2$,[1] phosphoramidite ligands (*Ra*,*RC*,*RC*)-**5**, (*Ra*,*RC*,*RC*)-**6** and (*Sa*,*SC*,*SC*)-**7** were prepared according to published procedures. [2] $Rh(acac)(CO)_2$ was purchased. All allylic carbonates (1a – 1f) were synthesized by the reaction of corresponding allylic alcohols with methyl chloroformate in the presence of pyridine. (*E*)-4-methoxycinnamyl alcohol, (*E*)-2-methoxycinnamyl alcohol, and (*E*)-3-(2-furanyl)-2-propen-1-ol were prepared by the $NaBH_4/CeCl_3$ reduction of corresponding aldehydes. (*E*)-cinnamyl alcohol, (*E*)-2-hexen-1-ol, (*E*)-2-penten-1-ol, 2-methoxycinnamaldehyde, (*E*)-3-(2-

[1] Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.
[2] Alexakis, A.; Rosset, S.; Allamand, J.; March, S.; Guillen, F.; Benhaim, C. *Synlett* **2001**,1375.

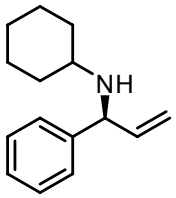
furyl)acrolein, (Aldrich Chemicals Co.), (*E*)-4-methoxycinnamaldehyde (TCI), (Alfa Aesar) were purchased and used without further purification.

General Procedure for iridium catalysed allylic aminations
Catalyst activation with propylamine.
$[Ir(cod)Cl]_2$ (0.04 mmol) and phosphoramidite ligand (**1**, **2** or **3**) (0.08 mmol.) were diluted in 0,3 ml of dry THF and 0.3 ml propylamine and the mixture was stirred under argon stream at 50 °C for 20 min. After this time all volatiles were evaporated. The yellow solid was diluted in 4ml of dry THF to generate a stock solution of the activated catalyst. Amine (1.2 mmol) was added to 1 ml of the stock solution of the catalyst (1 mol% catalyst). Carbonate (1 mmol) was added via syringe and the reaction was stirred at room temperature until the carbonate was fully converted (TLC analysis). The volatile materials were evaporated and the ratio of regioisomers (branched to linear b/l) was determined by ^1H – NMR of the crude mixture. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate or cyclohexane/MTBE) to give the desired product.



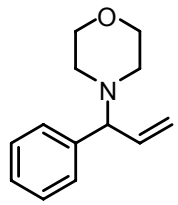
Benzyl-(1-phenyl-allyl)-amine
(Table 1, Entry 1), (6a) The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol), ligand **1** (9 mg, 0.02 mmol), cinnamyl methyl carbonate (192 mg, 1 mmol.) and benzylamine (214 mg, 2 mmol). The reaction was conducted at room temperature for 1.5h. ^1H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 90/10. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (129 mg, 58 %) as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 90 % [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 1 ml/min; detection wavelength = 254 nm; TR = 13.4 (-), 17.5 (+) min]. (R) configuration, $[\alpha]_D^{20}$ = -2.5 (c = 0.84, $CHCl_3$); **(Table 1, Entry 2), (6a)** The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol) Ligand **2** (11.4 mg, 0.02 mmol), cinnamyl methyl carbonate (192 mg, 1 mmol.) and benzylamine (214 mg, 2 mmol). The reaction was conducted at room temperature for 0.25 h. ^1H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 92/8. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (170 mg, 76 %) as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 94 % [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 1 ml/min; detection wavelength = 254 nm; TR = 13.4 (-), 17.5 (+) min]. (R)

configuration, $[\alpha]_D^{20}$ = -2.6 (c = 1.100, $CHCl_3$); **(Table 1, Entry 3), (6a)** The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol) Ligand **3** (11.4 mg, 0.02 mmol), cinnamyl methyl carbonate (192 mg, 1 mmol.) and benzylamine (214 mg, 2 mmol). The reaction was conducted at room temperature for 0.5 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 96/4. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (168 mg, 75 %) as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 98 % [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 1 ml/min; detection wavelength = 254 nm; TR = 13.4 (-), 17.5 (+) min]. (S) configuration, $[\alpha]_D^{20}$ = +2.8 (c = 1.35, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.40-7.20 (m, 10H), 5.95 (ddd, 1H, *J* = 7.3 Hz, *J* = 10.1 Hz, *J* = 17.2 Hz), 5.22 (d, 1H, *J* = 17.1 Hz), 5.12 (d, 1H, *J* = 10.2 Hz), 4.22 (d, 1H, *J* = 7.1 Hz), 3.73 (d, 2H, *J* = 3.1 Hz), 1.85 (bs, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 142.9,141,1, 140.8, 128.5, 128.3, 128.2, 127.3, 127.2, 126.9, 115.2, 65.0, 51.2; Analytical data fits with literature.[3]



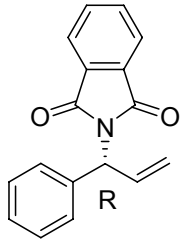
***N*-(1-phenylallyl)cyclohexanamine (Table 1, Entry 4), (6b)**
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (13 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), cinnamyl methyl carbonate (384 mg, 2 mmol) and cyclohexylamine (218 mg, 2.4 mmol). The reaction was conducted at room temperature for 46h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 94/6. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 6/1) to give the title compound (319 mg, 74 %) as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 97% [Diacel Chiralcel OJ (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 98/2; flow rate = 0.3 mL/min; detection wavelength = 215 nm; TR = 14.6 (+), 15.3 (-) min].
$[\alpha]_D^{20}$ = -14.3 (c = 0.700, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32 (d, *J* = 4.33 Hz, 1H), 7.25-7.20 (m, 1H), 5.92 (ddd, *J* = 17.18, 10.12, 7.13 Hz, 1H), 5.15 (d, *J* = 17.10 Hz, 1H), 5.07 (d, *J* = 10.10 Hz, 1H), 4.38 (d, *J* = 7.11 Hz, 1H), 2.35-2.45 (m, 1H), 1.94 (d, *J* = 12.79 Hz, 1H), 1.84 (d, *J* = 12.69 Hz, 1H), 1.64-1.74 (m, 2H), 1.52-1.61 (m, 1H), 1.32 (br, 1H), 1.11 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.4 (C), 141.6 (CH), 128.4 (CH), 127.2 (CH), 126.9 (CH), 114.5 (CH_2), 62.3 (CH), 53.4 (CH), 34.0 (CH_2), 33.7 (CH_2), 26.2 (CH_2), 25.1 (CH_2), 25.05 (CH_2); HRMS: m/z (FAB) calc for $C_{15}H_{21}N$ (M^+) 215.1675, found 215.1634; IR(film): ν [cm^{-1}] = 3061(w), 3025(w), 2925(s), 2851(s), 1450(s), 1115(m), 700(s);

[3] T. Ohmura, J.F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 15164-15165.



4-(1-phenylallyl)morpholine (Table 1, Entry 5), (6c)

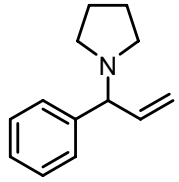
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol), cinnamyl methyl carbonate (180 mg, 0.93 mmol) and morpholine (105 mg, 1.2 mmol). The reaction was conducted at room temperature for 16h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 95/5. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 6/1) to give the title compound (155 mg, 82 %) as colourless oil. HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel Chiralcel OJ (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 98.4/1.6; flow rate = 1 mL/min; detection wavelength = 215 nm; TR = 6.7 (+), 7.5 (-) min]. $[\alpha]_D^{20}$ = -94 (c = 1.022, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.34-7.27 (m, 4H), 7.24-7.20 (m, 1H), 5.89 (ddd, 1H, *J* = 9.5 Hz, *J* = 9.5 Hz, *J* = 17.3 Hz), 5.22 (d, 1H, *J* = 17.0 Hz), 5.09 (dd, 1H, *J* = 1.1 Hz, *J* = 10. 1Hz), 3.67 (t, 4H, *J* = 4.6 Hz), 3.60 (d, 1H, *J* = 8.8 Hz), 2.46 (bs, 2H), 2.34-2.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 147.6 (s, 1C), 140.1 (s, 1C), 129.1 (s, 1C), 117.0 (s, 1C), 114.9 (s, 1C), 113.2 (s, 1C), 55.6 (s, 1C), 38.0 (s, 1C), 19.1 (s, 1C), 13.9 (s, 1C). Analytical data fits with literature.[4]



2-((R)-1-phenylallyl)isoindoline-1,3-dione (Table 1, Entry 6), (6d)

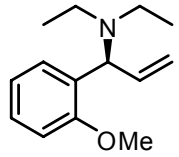
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (13 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), cinnamyl methyl carbonate (384 mg, 2 mmol) and phthalimide (441 mg, 3 mmol). The reaction was conducted at room temperature for 12 h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 98/2. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 6/1) to give the title compound (347 mg, 66 %) as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 98% [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 7.7 (+), 8.8 (-) min]. $[\alpha]_D^{20}$ = - 45.4 (0.87, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.82 (dd, 1H, *J* = 3.0 Hz, *J* = 5.4 Hz) , 7.68 (dd, 1H, *J* = 3.0 Hz, *J* = 5.4 Hz), 7.46 (d, 1H, *J* = 7.5 Hz), 7.34 (dd, 1H, *J* = 7.4 Hz, *J* = 7.4 Hz), 7.27 (dd, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 6.67 (ddd, 1H, *J* = 7.6 Hz, *J* = 10 Hz, *J* = 17.2 Hz), 5.98 (d, 1H, *J* = 7.6 Hz), 5.39 (d, 1H, *J* = 10.2 Hz,), 5.36 (d, 1H, *J* = 17.1 Hz);

^{13}C NMR (101 MHz, $CDCl_3$ δ ppm 167.6, 138.4, 134.0, 133.9, 131.8, 128.4, 127.7, 127.6, 123.2, 119.0, 56.7; Analytical data fits with literature.[4]



1-(1-phenylallyl)pyrrolidine (Table 1, Entry 7), (6e)

The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (12 mg, 0.02 mmol), cinnamyl methyl carbonate (192 mg, 1 mmol) and pyrrolidine (86 mg, 1.2 mmol). The reaction was conducted at room temperature for 0.5 h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 95/5. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (136 mg, 73 %) as colourless oil. HPLC analysis indicated that the enantiomeric excess of the product was 98 % [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 0.4 mL/min; detection wavelength = 215 nm; TR = 13.0 (-), 15.2 (+) min]. $[\alpha]_D^{20}$ = -1.1 (c = 1.000, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.35-7.27 (m, 4H), 7.24-7.19 (m, 1H), 6.02 (ddd, 1H, *J* = 9.0 Hz, *J* = 9.8 Hz, *J* = 17.1 Hz), 5.19 (d, 1H, *J* = 17.0 Hz), 4.99 (dd, 1H, *J* = 1.2 Hz, *J* = 10.1 Hz), 3.57 (d, 1H, *J* = 8.6 Hz), 2.52-2.46 (m, 2H), 2.39-2.33 (m, 2H), 1.78-1.71 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.2 (s, 1C), 141.5 (s, 1C), 128.4 (s, 1C), 127.6 (s, 1C), 127.0 (s, 1C), 114.8 (s, 1C), 75.2 (s, 1C), 52.9 (s, 1C), 23.3 (s, 1C). Analytical data fits with literature.[4]

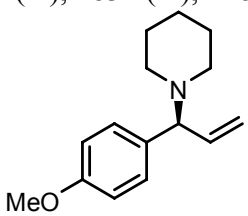


***N,N*-diethyl-1-(2-methoxyphenyl)prop-2-en-1-amine (Table 1, Entry 8), (6f)**

The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (11 mg, 0.015 mmol), ligand **2** (17 mg, 0.030 mmol, 0.02 equiv.), (*E*)-3-(2-methoxyphenyl)allyl methyl carbonate (335 mg, 1.5 mmol) and diethylamine (79 mg, 1.8 mmol). The reaction was conducted at room temperature for 18h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 96/4. The mixture was purified by column chromatography on silica gel (cyclohexane/ethyl acetate = 3/1) to give the title compound (205 mg, 62 %) as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 91% [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 1 mL/min; detection wavelength = 215 nm; TR = 7.2 (-), 8.0 (+) min]. $[\alpha]_D^{20}$ = -73.0 (c = 1.004, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (dd, *J* = 7.57, 1.39 Hz, 1H), 7.23-7.16 (m, 1H), 6.95 (t, *J* = 7.40, 7.40 Hz, 1H), 6.86 (d, *J* = 8.19 Hz, 1H), 5.91 (ddd, *J* = 17.38, 9.82, 8.76 Hz, 1H), 5.22 (dd, *J* = 17.04, 0.90 Hz, 1H), 4.99 (dd, *J* = 10.04, 1.59 Hz, 1H), 4.67 (d, *J* = 8.50 Hz, 1H), 3.82 (s, 3H), 2.68-2.53 (m, 4H), 0.97 (t, *J* = 7.08, 7.08 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.1 (C), 140.8 (CH), 131.0 (C), 128.5 (CH), 127.4 (CH), 120.6

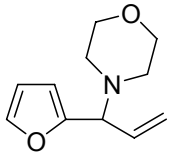
[4] Weihofen R.; Tverskoy O.; Helmchen G., *Angew. Chem. Int. Ed.*, **2006**, 45, 5546.

(CH), 114.5 (CH_2), 110.8 (CH), 61.1 (CH), 55.5 (CH), 42.6 (2xCH_2), 10.8 (2xCH_3); HRMS: m/z (FAB) calc for $C_{14}H_{21}NO$ (M^+) 219.1623, found 219.1621. IR(film): ν [cm^{-1}] = 3076 (w), 2968 (s), 2943 (s), 2871(m), 2834 (m), 1488 (s), 1464 (s), 1239 (s), 754 (s).



***N*-1-(1-(4-methoxyphenyl)allyl)piperidine (Table 1, Entry 9), (6g)**

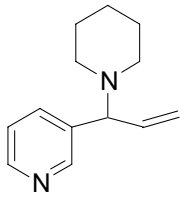
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (26 mg, 0.04 mmol), ligand **2** (45 mg, 0.08 mmol), (*E*)-3-(4-methoxyphenyl)allyl methyl carbonate (888 mg, 4 mmol.) and piperidine (374 mg, 4.4 mmol). The reaction was conducted at room temperature for 46h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 91/9. The mixture was purified by column chromatography on silica gel (cyclohexane/ethyl acetate/triethylamine = 3/1/0.01) to give the title compound (863 mg, 91 %) as yellowish solid. HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 16.1 (-), 17.8 (+) min]. $[\alpha]_D^{20}$ = -102.5 (c = 1.012, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.37-1.45 (m, 2H), 1.50-1.59 (m, 4H), 2.33-2.20 (m, 2H), 2.36-2.48 (m, 2H), 3.61 (d, *J* = 8.59 Hz, 1H), 3.79 (s, 3H), 5.06 (d, *J* = 10.09 Hz, 1H), 5.15 (d, *J* = 17.40 Hz, 1H) 5.94 (ddd, *J* = 17.40, 10.09, 8.59 Hz, 1H), 6.85 (d, *J* = 8.60 Hz, 2H), 7.24 (d, *J* = 8.60 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$ δ ppm 158.6 (C), 140.73 (CH), 134.5 (C), 129.07 (2xCH), 115.64 (CH_2), 113.84 (2xCH), 74.8 (CH), 55.3 (CH_3), 52.6 (2xCH_2), 26.3 (2xCH_2), 24.8 (CH_2); HRMS: m/z (FAB) calc for $C_{14}H_{21}NO$ (M^+) 231.1623, found 231.1625; IR(KBr): ν [cm^{-1}] = 2963 (s), 2934 (s), 2851 (m), 2783 (s), 2744 (m), 1609 (m), 1510 (s), 1253 (s), 1030 (s), 834 (s), 803 (s).



4-(1-furan-2-yl-allyl)-morpholine (Table 1, Entry 10), (6h)

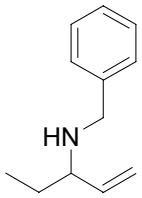
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (13.5 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), (*E*)- 3-furan-2-yl-prop-2-en-1-ol methyl carbonate (365 mg, 2 mmol.) and morpholine (350 mg, 4 mmol). The reaction was conducted at room temperature for 20 h. ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 95/5. The mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate = 9/1) to give the title compound (313 mg, 81 %) as yellowish oil. Enantiomers could not be separated on any of available columns. $[\alpha]_D^{20}$ = -54.5 (c = 0.915, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.37 (s, 1H), 6.30 (m, 1H), 6.18 (d, 1H, J=3.0Hz), 6.00 (ddd, 1H, J=8.5Hz, J=10.0Hz, J=18.0Hz), 5.25 (m, 2H), 3.89 (d, 1H, J=8.2Hz),3.69 (t, 4H, J=4.7Hz), 2.50 (m, 2H) ppm 2.35 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 135.4, 118.7, 110.1, 108.2, 67.4, 67.2, 51.2; HRMS: m/z (FAB) calc for $C_{11}H_{15}NO_2$ (M^+) 193.1103, found 193.1077; IR(film): ν [cm^-

^{1}] = 3106 (w), 3080 (w), 2955 (s), 2863 (s), 2810 (s), 1641 (w), 1497 (m), 1457 (m), 1310 (m), 1122 (vs), 1004 (vs), 925 (s).



3-(1-piperidin-1-yl-allyl)-pyridine (Table 1, Entry 11), (6i)

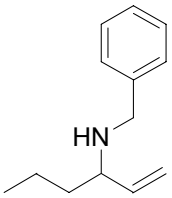
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (13.5 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), (*E*)- 3-pyridin-3-yl-prop-2-en-1-ol methyl carbonate (396 mg, 2 mmol.) and piperidine (340 mg, 4 mmol). The reaction was conducted at room temperature for 0.5h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 96/4. The mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate = 1/1) to give the title compound (345 mg, 85 %) as colourless oil. HPLC analysis indicated that the enantiomeric excess of the product was 99 % [Diacel Chiralcel OD-H (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 95/5; flow rate = 1 ml/min; detection wavelength = 254 nm; TR = 6.9 (-), 8.0 (+) min]. $[\alpha]_D^{20}$ = -65 (c = 1.060, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.52 (s, 1H), 8.44 (d, 1H, *J* = 4.6 Hz), 7.64 (d, 1H, *J* = 7.8 Hz), 7.21 (dd, 1H, *J* = 4.8 Hz, *J* = 7.8 Hz), 5.92-5.83 (m, 1H), 5.18 (d, 1H, *J* = 17.1 Hz), 5.11 (d, 1H, *J* = 10.1 Hz), 3.71 (d, 1H, *J* = 8.6 Hz), 2.41-2.22 (m, 4H), 1.55-1.49 (m, 4H), 1.41-1.36 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 149.7, 148.3, 139.0, 137.6, 135.3, 123.3, 116.9, 72.6, 52.2, 26.1, 24.5**;** HRMS: m/z (ESI) calc for $C_{13}H_{19}N_2$ ($M+H^+$) 203.15428, found 203.15425; IR(film): ν [cm^{-1}] = 3461 (m), 2942 (vs), 2843 (vs), 2784 (vs), 2751 (vs), 2357 (w), 1845 (w), 1653 (m), 1574 (vs), 1418 (vs), 1313 (s), 1109 (vs), 991 (vs), 925 (vs).



Benzyl-(1-ethyl-allyl)-amine (Table 1, Entry 12), (6j)

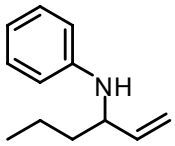
The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (13.5 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), (*E*)- pent-2-en-1-ol methyl carbonate (290 mg, 2 mmol.) and benzylamine (430 mg, 4 mmol). The reaction was conducted at room temperature for 5h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 91/9. The mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate = 5/1) to give the title compound (218 mg, 62 %) as colourless oil. HPLC analysis indicated that the enantiomeric excess of the product was 98 % [Diacel Chiralcel OJ (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99/1; flow rate = 1 ml/min; detection wavelength = 254 nm; TR = 7.8 (-), 8.6 (+) min]. $[\alpha]_D^{20}$ = -2.5 (c = 1.040, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.32-7.28 (m, 4H), 7.25-7.20 (m, 1H), 5.60 (ddd, 1H, *J* = 8.3 Hz, *J* = 10.2 Hz, *J* = 17.3 Hz), 5.16-5.07 (m, 2H), 3.82 (d, 1H, *J* = 13.2 Hz), 3.64 (d, 1H, *J* = 13.2 Hz), 2.93 (dd, 1H, *J* = 7.9 Hz, *J* = 13.5 Hz), 1.59-1.39 (m, 3H), 0.87 (t, 3H, *J* = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 141.0, 140.7,

128.3, 128.1, 126.8, 116.3, 62.8, 51.21, 28.4, 10.3; HRMS: m/z (FAB) calc for $C_{13}H_{19}N$ (M^+) 189.1517, found 189.1525; IR(film): ν [cm^{-1}] = 3060 (m), 2962 (m), 2935 (m), 1451 (s), 1390 (m), 1102 (s), 912 (vs), 708 (vs).



Benzyl-(1-propyl-allyl)-amine (Table 1, Entry 13), (6k)

The general procedure for allylic aminations was followed with $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol), ligand **2** (11.4 mg, 0.02 mmol), (*E*)- hex-2-en-1-ol methyl carbonate (145 mg, 1 mmol.) and benzylamine (214 mg, 2 mmol). The reaction was conducted at room temperature for 2h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 89/11. The mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate = 4/1) to give the title compound (114 mg, 60 %) as colourless oil. HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel Chiralcel OJ (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99/1; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 7.2 (-), 8.1 (+) min]. $[\alpha]_D^{20}$ = -1.0 (c = 1.072, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.32-7.28 (m, 4H), 7.25-7.20 (m, 1H), 5.61 (ddd, 1H, *J* = 8.3 Hz, *J* = 10.2 Hz, *J* = 17.2 Hz), 5.15-5.06 (m, 2H), 3.82 (d, 1H, *J* = 13.1 Hz), 3.63 (d, 1H, *J* = 13.2 Hz), 3.01 (dd, 1H, *J* = 7.7 Hz, *J* = 13.7 Hz), 1.48-1.22 (m, 5H), 0.88 (t, 1H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 141.4, 140.7, 128.3, 128.1, 126.7, 115.9, 60.9, 51.2, 37.9, 19.1, 14.0; Analytical data fits with literature.[4]



***N*-(hex-1-en-3-yl)aniline (Table 1, Entry 14), (6l)**

The general procedure for allylic amination was followed with $[Ir(cod)Cl]_2$ (28 mg, 0.04 mmol), ligand **2** (45 mg, 0.02 mmol), (*E*)-hex-2-enyl methyl carbonate (318 mg, 2 mmol) and aniline (204 mg, 2.2 mmol). The reaction was conducted at room temperature for 46h. ^{1}H-NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 95/5. The mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 20/1) to give the title compound (271 mg, 77 %) as colourless oil. HPLC analysis indicated that the enantiomeric excess of the product was 91% [Diacel Chiralcel OJ (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 99.6/0.4; flow rate = 1 mL/min; detection wavelength = 215 nm; TR = 7.2 (-), 8.0 (+) min]. $[\alpha]_D^{20}$ = -7.044 (c = 0.530, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.15 (t, *J* = 7.89, 7.89 Hz, 2H), 6.67 (t, *J* = 7.30, 7.30 Hz, 1H), 6.60 (d, *J* = 7.77 Hz, 2H), 5.74 (ddd, *J* = 16.75, 10.28, 6.19 Hz, 1H), 5.21 (d, *J* = 17.21 Hz, 1H), 5.11 (d, *J* = 10.29 Hz, 1H), 3.81 (q, *J* = 6.44, 6.42, 6.42 Hz, 1H), 3.70 (bs, 1H), 1.63-1.53 (m, 2H), 1.50-1.38 (m, 2H), 0.95 (t, *J* = 7.26, 7.26 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 147.6 (C), 140.1 (CH), 129.1 (CH), 117.0

(CH), 114.9 (CH_2), 113.2 (CH), 55.6 (CH), 38.0 (CH_2), 19.1 (CH_2), 14.0 (CH_3); Analytical data fits with literature.[5]

General Procedures for iridium catalyzed Allylic Alkylations.

Catalyst activation with DABCO. General procedure A
In a schlenck tube $[Ir(cod)Cl]_2$ (0.02 equiv.), phosphoramidite ligand **2** (0.04 equiv.) and DABCO (0.2 equiv.) were dissolved in dry THF (1 ml/mmol) and stirred under argon atmosphere at 50 °C for 2 hours. Carbonate (1 equiv.) was added in one portion and the mixture was stirred for another 20 minutes. Nucleofile (Cyanoacetate) was added and the mixture was stirred at 50 °C until TLC showed full conversion. The reaction was quenched with saturated NH_4Cl solution and the aqueous layer was extracted with CH_2Cl_2. Collected organic extracts were dried over $MgSO_4$, filtered and volatiles were evaporated in *vacuo*. The ratio of diastereoisomers (sin/anti) was determined by ^1H – NMR of the crude reaction mixture. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate or cyclohexane/MTBE) to give the desired product.

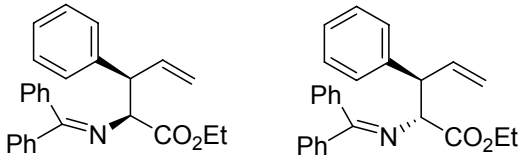
Catalyst activation with propylamine. General procedure B
$[Ir(cod)Cl]_2$ (0.08 mmol) and phosphoramidite ligand **2** (0.16 mmol.) were diluted in 1 ml of dry THF, 0.3 ml propylamine were added and the mixture was stirred under argon stream at 50 °C for 20 min. After this time all volatiles were evaporated. The yellow solid was diluted in 4ml of dry THF to generate a stock solution of the activated catalyst. Amine (1.2 mmol) was added to 1 ml of the stock solution of the catalyst (2 mol% catalyst). Carbonate (1 mmol) was added in one portion and the reaction was stirred at room temperature until TLC showed full conversion. The volatile materials were evaporated and the ratio of diastereoisomers (sin/anti) was determined by ^1H – NMR of the crude reaction mixture. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate or cyclohexane/MTBE) to give the desired product.

LiHMDS as a base. General procedure C
$[Ir(cod)Cl]_2$ (0.02 mmol, 0.02 equiv.), phosphoramidite ligand **2** (0.04 mmol, 0.04 equiv.) and carbonate (1 mmol, 1 equiv.) were dissolved in dry THF (1mL) and stirred under argon atmosphere at r.t. for 15 minutes. In a separate flask solution of cyanoacetate or benzophenone protected glycine ethylester (1.1 mmol, 1.1 equiv.) in dry THF (2 mL) was cooled to -78°C. LiHMDS (1.1 mmol, 1.1 equiv.) was added dropwise via syringe and solution was stirred for 30 minutes at -78°C. The solution containing lithium enolate was added dropwise to a solution containing carbonate and catalyst cooled to -78 °C. The reaction mixture was allowed to warm up to room temperature and was stirred until TLC showed full conversion. Reaction mixture was quenched with 20 mL of sat. NH_4Cl solution, extracted with CH_2Cl_2 (4x10mL), washed with brine, dried over $MgSO_4$, filtered and evaporated. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE) to give the desired product.

[5] Leitner, A.; Shu, C. T.; Hartwig, J. F.*Org. Lett.* **2005**, 7, (6), 1093-1096.

KOH or NaOH as a base. General procedure D

$[Ir(cod)Cl]_2$ (0.02 mmol, 0.02 equiv.), and phosphoramidite ligand **2** (0.04 mmol, 0.08 equiv.) were dissolved in 1 mL of dry THF and stirred under argon atmosphere at r.t. for 15 min.. In a separate flask cyanoacetate or benzophenone protected glycine ethylester (1.1 mmol, 1.1 equiv.), KOH (1.1 mmol, 1.1 equiv.) or NaOH (1.1 mmol, 1.1 equiv.) and Bu_4NHSO_4 (0.1 mmol, 0.1 equiv.) were suspended in dry THF and stirred vigorously for 30 minutes at 0 °C. The solution containing the catalyst was cooled to 0 °C and carbonate (1 mmol, 1 equiv.) was added dropwise via syringe, suspension containing the enolate was subsequently added and the reaction mixture was allowed to warm to room temperature. The reaction was conducted at r.t until TLC showed full conversion. Reaction mixture was quenched with 20 mL of sat. NH_4Cl solution, extracted with CH_2Cl_2 (4x10mL), washed with brine dried over $MgSO_4$, filtered and evaporated. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE) to give the desired product.



9a **10a**

(2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate (9a).
(2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate (10a).

DABCO as a base, Ligand 2, (Table 2, Entry 1).

The general procedure A was followed with cinnamyl methylcarbonate (96 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 16 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =25/1) to give (103 mg, 54 % yield) of the **9a** and (63 mg, 33 % yield) of the **10a**.

9a: $[\alpha]_D^{20}$ = -175.4 (c = 0.960, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 97 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 5 min. (-), 5.9 min (+)]; **10a:** $[\alpha]_D^{20}$ = +168.7 (c = 1.230, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 95 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 4.8 (-), 7.1 (+) min].

LiHMDS as a base, Ligand 1, (Table 2, Entry 2).

The general procedure C was followed with cinnamyl methylcarbonate (96 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **1** (11 mg, 0.02 mmol) and LiHMDS (0.5 ml, 1M solution in THF) in dry THF (3 mL). The reaction was conducted at r.t. for 3h. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =25/1) to give (107 mg, 56 % yield) of the **9a** and (46 mg, 24 % yield) of the **10a**.

9a: $[\alpha]_D^{20}$ = -89.6 (c = 0.742, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 65 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 5.0 (-), 5.9 min (+)]. **10a:** $[\alpha]_D^{20}$ = +119.6 (c = 0.945, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 62 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 4.7 (-), 7.1 min (+)].

LiHMDS as a base, Ligand 2, (Table 2, Entry 3).

By a similar procedure as above in the presence of ligand **2** cinnamyl methylcarbonate (96 mg, 0.5 mmol) was transformed into (121 mg, 63 % yield) of the **9a** and (40 mg, 21 % yield) of the **10a**. The reaction was conducted at r.t. for 3h.

9a: $[\alpha]_D^{20}$ = -172.4 (c = 0.560, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 87 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 5.0 (-), 5.9 min (+)]. **10a:** ee not determined.

KOH as a base, Ligand 2, (Table 2, Entry 4).

The general procedure D was followed with cinnamyl methylcarbonate (96 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 48 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =25/1) to give (50 mg, 26 % yield) of the **9a** and (75 mg, 39 % yield) of the **10a**.

Base free conditions, Ligand 2, (Table 2, Entry 4).

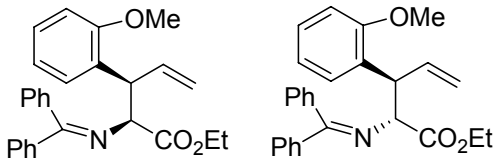
The general procedure B was followed with cinnamyl methylcarbonate (96 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol) were added to a solution of $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol) and ligand **2** (11 mg, 0.02 mmol) activated by propylamine. The reaction was conducted at r.t. for 7 days but yielded in no product.

9a: $[\alpha]_D^{20}$ = -170.5 (c = 0.89, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 91 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 5.0 (-), 5.8 (+) min]. **10a:** ee not determined.

9a: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.64 (d, 2H, J = 7.2 Hz), 7.42-7.30 (m, 6H), 7.24-7.10 (m, 5H), 6.79 (d, 2H, J = 6.2 Hz), 6.32 (ddd, 1H, J = 8.9 Hz, J = 13.5 Hz, J = 16.9 Hz), 5.22-5.16 (m, 2H), 4.35 (d, 1H, J = 6.0 Hz), 4.17-4.02 (m, 3H), 1.12 (t, 3H, J = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.1, 170.8, 140.9, 139.5, 137.4, 136.2, 130.3, 128.9, 128.5, 128.4, 128.2, 127.9, 127.7, 126.6, 117.4, 70.6, 60.8, 53.7, 14.1; HRMS: m/z (ESI) calc for $C_{26}H_{26}NO_2$ ($M+H^+$) 384.19581, found 384.19616; IR(film): ν [cm^{-1}] = 3054 (m), 2981 (s), 2922 (vs), 2850 (s), 1963 (w), 1878 (w), 1733 (vs), 1615 (s), 1444 (s), 1240 (s), 1024 (s), 703 (s).

10a: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.43 (d, 2H, *J* = 7.3 Hz), 7.39-7.29 (m, 4H), 7.26-7.07 (m, 7H), 6.71 (d, 2H, *J* = 3.8 Hz), 5.97 (ddd, 1H, *J* = 8.9 Hz, *J* = 10.1 Hz, *J* = 17.3 Hz), 5.11 (d, 1H, *J* = 17.1 Hz), 5.05 (d, 1H, *J* = 10.2 Hz), 4.33 (d, 1H, *J* = 9.1 Hz), 4.22-4.08 (m, 3H), 1.23 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.1, 170.9, 140.3, 139.6, 137.5, 135.9, 130.1, 128.9, 128.9, 128.6, 128.2, 128.2, 128.0, 127.8,

126.6, 116.9, 70.9, 60.9, 54.1, 14.2; HRMS: m/z (ESI) calc for $C_{26}H_{26}NO_2$ ($M+H^+$) 384.19581, found 384.19630; IR(film): ν [cm^{-1}] = 3050 (m), 2985 (s), 2922 (vs), 2850 (s), 1960 (w), 1876 (w), 1730 (vs), 1615 (s), 1448 (s), 1240 (s), 1120 (s), 1024 (s), 703 (s).



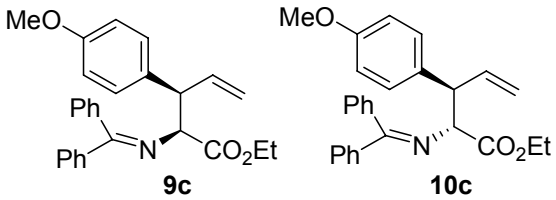
9b **10b**

(2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-(2-methoxyphenyl)pent-4-enoate, (9b) (2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-(2-methoxyphenyl)pent-4-enoate, (10b), (Table 3, Entry 1).

The general procedure A was followed with (*E*)-3-(2-methoxyphenyl)allyl methyl carbonate (111 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 48 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =20/1) to give (118 mg, 57 % yield) of the **9b** and (52 mg, 25 % yield) of the **10b**.

9b: $[\alpha]_D^{20}$ = -170.5 (c = 0.89, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 91 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 98/2; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 7.6 (-), 8.3 (+) min]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.58 (d, 2H, *J* = 7.2 Hz), 7.37-7.25 (m, 6H), 7.12 (t, 2H, *J* = 7.9 Hz), 6.79 (t, 1H, *J* = 7.3 Hz), 6.71-6.65 (m, 3H), 6.42 (dt, 1H, *J* = 9.6Hz, *J* = 17.3 Hz), 5.22 (d, 1H, *J* = 17.3 Hz), 5.17 (dd, 1H, *J* = 1.1 Hz, *J* = 10.2 Hz), 4.54 (d, 1H, *J* = 5.5 Hz), 4.47 (dd, 1H, *J* = 5.6 Hz, *J* = 8.7 Hz), 4.17-4.00 (m, 2H), 3.50 (s, 3H), 1.13 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.3, 170.8, 156.7, 139.6, 136.7, 136.4, 130.1, 129.6, 129.2, 128.8, 128.1, 127.9, 127.9, 127.5, 120.1, 117.5, 110.3, 67.8, 60.6, 54.9, 47.6, 14.1; HRMS: m/z (ESI) calc for $C_{27}H_{28}NO_3$ ($M+H^+$) 414.20637, found 414.20594; IR(film): ν [cm^{-1}] = 3073 (m), 2968 (s), 2929 (s), 2830 (m), 2265 (m), 1746 (vs), 1661 (s), 1635 (vs), 1490 (vs), 1457 (s), 1420 (s), 1326 (m), 1286 (m), 1155 (m), 1024 (m), 912 (s), 754 (vs), 689 (vs).

10b: $[\alpha]_D^{20}$ = -136.5 (c = 1.15, $CHCl_3$); ee not determined; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.41-7.33 (m, 5H), 7.29 (t, 1H, *J* = 7.3 Hz), 7.21 (t, 2H, *J* = 7.5 Hz), 7.13-7.05 (m, 2H,), 6.85-6.77 (m, 2H), 6.69 (d, 1H, *J* = 8.1 Hz), 6.11 (dt, 1H, *J* = 9.8Hz, *J* = 18.3 Hz), 5.13 (d, 1H, *J* = 17.1 Hz), 5.01 (d, 1H, *J* = 10.1 Hz), 4.62 (d, 1H, *J* = 9.4 Hz), 4.44 (t, 1H, *J* = 9.0 Hz), 4.27-4.10 (m, 2H), 3.56 (s, 3H), 1.25 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.5, 170.4, 157.0, 140.1, 137.0, 136.0, 130.2, 129.9, 128.9, 128.5, 128.5, 127.9, 127.7, 127.6, 120.2, 116.7, 110.3, 69.3, 60.7, 54.8, 49.9, 14.2; HRMS: m/z (ESI) calc for $C_{27}H_{28}NO_3$ ($M+H^+$) 414.20637, found 414.20602; IR(film): ν [cm^{-1}] = 3070 (m), 2954 (s), 2929 (s), 2834 (m), 2265 (m), 1743 (vs), 1640 (vs), 1485 (vs), 1420 (s), 1320 (m), 1241 (m), 1155 (m), 1024 (m), 912 (s), 754 (vs), 696 (vs).

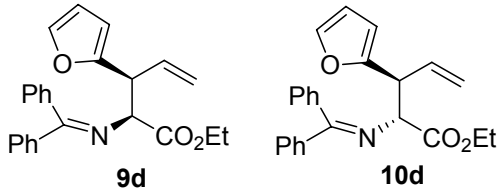


(2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-(4-methoxyphenyl)pent-4-enoate, (9c) (2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-(4-methoxyphenyl)pent-4-enoate, (10c) (Table 3, Entry 2).

The general procedure A was followed with (*E*)-3-(4-methoxyphenyl)allyl methyl carbonate (111 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 48 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =20/1) to give (110 mg, 54 % yield) of the **9c** and (89 mg, 43 % yield) of the **10c**.

9c: $[\alpha]_D^{20}$ = -145.2 (c = 0.515, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 94 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 6.1 (-), 7.9 min (+)]; **10c:** $[\alpha]_D^{20}$ = +84.3 (c = 0.865, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 91 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 6.2 (-), 7.9 (+) min].

9c: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.61 (d, 2H, *J* = 7.3 Hz), 7.40-7.27 (m, 6H), 7.01 (d, 2H, *J* = 8.6 Hz), 6.81 (d, 2H, *J* = 6.0 Hz), 6.73 (d, 1H, *J* = 8.6 Hz), 6.28-6.17 (m, 1H), 5.16-5.08 (m, 2H), 4.28 (d, 1H, *J* = 6.2 Hz), 4.10-3.99 (m, 3H), 3.73 (s, 3H), 1.10 (t, 3H, *J* = 7.1 Hz), ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.0, 170.9, 158.2, 137.7, 136.3, 132.9, 130.3, 129.5, 128.9, 128.4, 128.3, 127.9, 127.8, 117.0, 113.6, 70.8, 60.8, 55.2, 52.8, 14.1; HRMS: m/z (ESI) calc for $C_{27}H_{28}NO_3$ ($M+H^+$) 414.20637, found 414.20568; IR(film): ν [cm^{-1}] = 3050 (s), 2975 (s), 2929 (s), 1920 (w), 1872 (w), 1740 (vs), 1621 (vs), 1510 (vs), 1444 (s), 1240 (s), 1120 (s), 1030 (s), 918 (s), 695 (m); **10c:** ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.45 (d, 1H, *J* = 7.3 Hz), 7.40-7.29 (m, 4H), 7.26-7.21 (m, 2H), 7.03 (d, 2H, *J* = 8.6 Hz), 6.78-6.71 (m, 4H), 5.93 (ddd, 1H, *J* = 8.6 Hz, *J* = 10.1 Hz, *J* = 17.3 Hz), 5.08 (d, 1H, *J* = 17.1 Hz), 5.02 (d, 1H, *J* = 10.3 Hz), 4.29 (d, 1H, *J* = 8.9 Hz), 4.20-4.03 (m, 3H), 3.74 (s, 3H), 1.23 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.7, 171.1, 158.2, 137.8, 136.0, 132.4, 130.1, 129.8, 128.9, 128.5, 128.2, 128.0, 127.8, 116.5, 113.5, 70.9, 60.8, 55.2, 53.2, 14.2; HRMS: m/z (ESI) calc for $C_{27}H_{28}NO_3$ ($M+H^+$) 414.20637, found 414.20600; IR(film): ν [cm^{-1}] = 3045 (s), 2972 (s), 2929 (s), 1920 (w), 1830 (w), 1733 (vs), 1620 (vs), 1510 (vs), 1444 (s), 1220 (s), 1060 (s), 1030 (s), 918 (s), 695 (m).



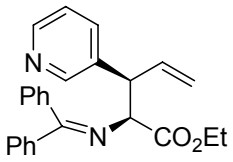
9d **10d**

(2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-(2-furyl)pent-4-enoate, (9d)
(2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-(2-furyl)pent-4-enoate, (10d)
(Table 3, Entry 3).

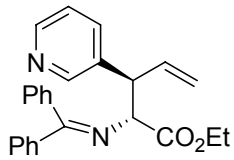
The general procedure A was followed with (*E*)-3-furan-2-yl-prop-2-en-1-ol methyl carbonate (91 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 48 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =20/1) to give (76 mg, 41 % yield) of the **9d** and (52 mg, 28 % yield) of the **10d**.

9d: $[\alpha]_D^{20}$ = -128.5 (c = 0.92, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 95 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 5.9 (-), 7.0 min (+)]; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, 2H, *J* = 7.3 Hz), 7.41-7.34 (m, 4H), 7.32-7.26 (m, 2H), 7.22 (s, 1H), 6.96 (d, 1H, *J* = 3.6 Hz), 6.27-6.17 (m, 2H), 6.01 (d, 1H, *J* = 3.0 Hz), 5.27-5.20 (m, 2H), 4.45 (d, 1H, *J* = 5.4 Hz), 4.22 (dd, 1H, *J* = 5.6 Hz, *J* = 8.7 Hz), 4.19-4.07 (m, 2H), 1.19 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.5, 170.6, 154.1, 141.1, 139.6, 136.2, 134.7, 130.3, 128.9, 128.6, 128.3, 127.9, 127.8, 118.3, 110.2, 106.5, 68.5, 60.9, 47.5, 14.1; HRMS: m/z (ESI) calc for $C_{24}H_{24}NO_3$ ($M+H^+$) 374.17507, found 374.17511; IR(film): ν [cm^{-1}] = 3385 (w), 3080 (w), 3054 (w), 2981 (m), 2922 (w), 2340 (m), 1738 (vs), 1659 (s), 1444 8s9, 1254 (s), 1180 (m), 1142 (m), 932 (s), 702 (vs);

10d: $[\alpha]_D^{20}$ = +34.4 (c = 0.742, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 94 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 95/5; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 5.1 (-), 7.3 min (+)]; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.52 (d, 1H, *J* = 7.4 Hz), 7.41-7.22 (m, 4H), 7.29-7.22 (m, 3H), 6.93 (d, 2H, *J* = 4.4 Hz), 6.25 (s, 1H), 6.17 (d, 1H, *J* = 2.7 Hz), 5.88 (td, 1H, *J* = 9.4 Hz, *J* = 18.3 Hz), 5.14 (d, 1H, *J* = 17.1 Hz), 5.09 (d, 1H, *J* = 10.2 Hz), 4.35 (d, 1H, *J* = 8.1 Hz), 4.24 (t, 1H, *J* = 8.3 Hz), 4.16 (q, 2H, *J* = 7.1 Hz), 1.23 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.4, 170.6, 153.4, 141.2, 139.6, 135.9, 134.9, 130.3, 128.9, 128.6, 128.4, 128.0, 127.9, 117.8, 110.2, 107.3, 69.1, 60.9, 47.6, 14.2; HRMS: m/z (ESI) calc for $C_{24}H_{24}NO_3$ ($M+H^+$) 374.17507, found 374.17516; IR(film): ν [cm^{-1}] = 3380 (w), 3050 (w), 2952 (s), 2916 (w), 2352 (m), 1730 (vs), 1650 (s), 1645 (s), 1451 (m), 1319 (m), 1265 (vs), 1037 (m), 918 (s), 715 (s).



9e



10e

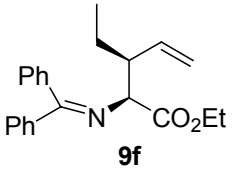
(2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-(3-purydyl)pent-4-enoate, (9e)
(2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-(3-purydyl)pent-4-enoate, (10e)
(Table 3, Entry 4).

The general procedure A was followed with (*E*)- 3-pyridin-3-yl-prop-2-en-1-ol methyl carbonate (100 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 48 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =20/1) to give (90 mg, 47 % yield) of the **9e** and (48 mg, 25 % yield) of the **10e**.

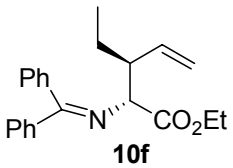
9e: $[\alpha]_D^{20}$ = +45.4 (c = 0.84, $CHCl_3$); HPLC analysis indicated that the enantiomeric excess of the product was 92 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 mm); heptane/2-propanol = 90/10; flow rate = 1 mL/min; detection wavelength = 254 nm; TR = 7.9 (major), 10.1 (minor) min].

^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.43-8.35 (m, 2H), 7.61 (d, 2H, *J* = 7.3 Hz), 7.44 (d, 2H, *J* = 7.9 Hz), 7.40-7.22 (m, 7H), 7.12 (dd, 1H, *J* = 4.8 Hz, *J* = 7.7 Hz), 6.78 (d, 2H, *J* = 6.1 Hz), 6.30 (ddd, 1H, *J* = 8.7 Hz, *J* = 10.1 Hz, *J* = 17.3 Hz), 5.23-5.13 (m, 2H), 4.30 (d, 1H, *J* = 5.8 Hz), 4.17-4.01 (m, 3H), 1.12 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ171.9, 170.8, 150.9, 148.2, 139.6, 136.6, 136.2, 136.0, 135.5, 130.9, 128.8, 128.5, 128.3, 128.0, 127.5, 123.5, 118.8, 70.9, 61.6, 50.8, 14.7; HRMS: m/z (ESI) calc for $C_{25}H_{25}N_2O_2$ ($M+H^+$) 385.19105, found 385.19128; IR(film): ν [cm^{-1}] = 3375 (w), 3080 (w), 3047 (m), 2981 (m), 2922 (m), 2850 (m), 2370 (m), 1740 (vs), 1661 (s), 1575 (s), 1444 (s), 1273 (s), 1175 (m), 1017 (m), 925 (s), 695 (vs).

10e: $[\alpha]_D^{20}$ = +34.4 (c = 0.98, $CHCl_3$); ee not determined; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.48-8.39 (m, 2H), 7.55 (d, 1H, *J* = 7.7 Hz), 7.47 (d, 2H, *J* = 7.4 Hz), 7.38 (m, 3H), 7.28-7.22 (m, 3H), 6.82 (d, 2H, *J* = 5.2 Hz), 5.99-5.88 (m, 1H), 5.13-5.04 (m, 2H), 4.36 (d, 1H, *J* = 8.0 Hz), 4.18-4.07 (m, 3H), 1.20 (t, 1H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.7, 170.4, 149.9, 147.9, 139.1, 136.6, 136.3, 136.1, 135.9, 130.5, 128.9, 128.6, 128.4, 128.0, 127.5, 123.1, 118.2, 70.0, 61.0, 50.9, 14.1; HRMS: m/z (ESI) calc for $C_{25}H_{25}N_2O_2$ ($M+H^+$) 385.19105, found 385.19150; IR(film): ν [cm^{-1}] = 3375 (w), 3080 (w), 2988 (m), 2922 (m), 2850 (m), 2352 (m), 1745 (vs), 1660 (s), 1576 (s), 1477 (m), 1444 (s), 1260 (s), 1175 (m), 1017 (m), 925 (s), 695 (vs).



9f



10f

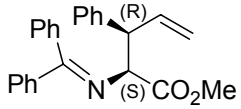
(2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-(ethyl)pent-4-enoate, (9f)

(2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-(ethyl)pent-4-enoate, (10f) (Table 3, Entry 5).

The general procedure A was followed with methyl (*E*)-pent-2-enyl carbonate (77 mg, 0.5 mmol), *N*-(diphenylmethylene)glycin ethylester (150 mg, 0.55 mmol), $[Ir(cod)Cl]_2$ (7 mg, 0.01 mmol), ligand **2** (11 mg, 0.02 mmol) and DABCO (12 mg, 0.1 mmol) in dry THF (3 mL). The reaction was conducted at 50 °C for 48 hours. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/EtOAc =20/1) to give (79 mg, 47 % yield) of the **9f** and (30 mg, 18 % yield) of the **10f**.

9f: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.63 (d, 2H, *J* = 7.2 Hz), 7.45-7.34 (m, 4H), 7.30 (t, 2H, *J* = 7.3 Hz), 7.12 (dd, 2H, *J* = 2.6 Hz, *J* = 6.4 Hz), 5.91 (dt, 1H, *J* = 9.9 Hz, *J* = 17.1 Hz), 5.14-5.08 (m, 2H), 4.15 (ddt, 2H, *J* = 3.6 Hz, *J* = 7.2 Hz, *J* = 10.6 Hz), 4.04 (d, 1H, *J* = 4.6 Hz), 2.63-2.59 (m, 1H), 1.34-1.20 (m, 5H), 0.77 (t, 3H, *J* = 7.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.7, 170.5, 139.7, 138.7, 136.6, 130.2, 128.9, 128.5, 128.4, 127.9, 127.9, 116.9, 69.2, 60.6, 50.1, 24.5, 14.3, 11.8; HRMS: m/z (ESI) calc for $C_{22}H_{26}NO_2$ ($M+H^+$) 336.19581, found 336.19591; IR(film): ν [cm^{-1}] = 3054 (m), 2968 (s), 2929 (s), 2863 (s), 2364 (w), 1976 (w), 1904 (w), 1733 (vs), 1621 (s), 1528 (m), 1451 (s), 1372 (m), 1319 (w), 1260 (m), 1030 (m), 912 (s), 695 (s).

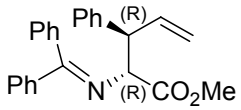
10f: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.63 (d, 2H, *J* = 7.3 Hz), 7.44-7.34 (m, 4H), 7.31 (t, 2H, *J* = 7.3 Hz), 7.11 (dd, 2H, *J* = 2.7 Hz, *J* = 6.4 Hz), 5.45 (dt, 1H, *J* = 9.8 Hz, *J* = 17.3 Hz), 5.07-4.98 (m, 2H), 4.12 (q, 2H, *J* = 7.1 Hz), 3.94 (d, 1H, *J* = 7.4 Hz), 2.72-2.62 (m, 1H), 1.66-1.46 (m, 2H), 1.22 (t, 3H, *J* = 7.1 Hz), 0.80 (t, 3H, *J* = 7.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.5, 170.9, 139.6, 138.4, 136.4, 130.3, 128.9, 128.6, 128.4, 127.9, 127.9, 117.2, 70.1, 60.6, 49.9, 23.3, 14.3, 11.7; HRMS: m/z (ESI) calc for $C_{22}H_{26}NO_2$ ($M+H^+$) 336.19581, found 336.19595; IR(film): ν [cm^{-1}] = 2965 (s), 2931 (s), 2863 (s), 2320 (w), 1976 (w), 1904 (w), 1825 (w), 1730 (vs), 1625 (s), 1515 (m), 1451 (s), 1312 (w), 1260 (m), 1030 (m), 925 (s), 695 (s).



(2S,3R)-methyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate (9a')

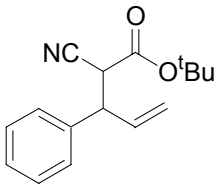
To a 20 ml of 1% K_2CO_3 solution in methanol was added (2S,3R)-ethyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate **9a**, 50 mg (0.13 mmol), and after 1h of stiring at room temperature, methanol was removed and the crude rest was purified by flash column chromatography on silica gel (cyclohexane/Ethylacetate =15/1) to give the title compound (40 mg, 89%) as colourless oil. $[\alpha]_D^{20}$ = - 206 (c = 1.12, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.64-7.61 (m, 2H), 7.45-7.10 (m, 11H), 6.74 (s, 2H), 6.30 (ddd, 2H, *J* = 8.9 Hz, *J* = 10.0 Hz, *J* =17.1 Hz), 5.21 (d, 1H, *J* = 10.0 Hz), 5.17 (d, 1H, *J* = 17.1 Hz), 4.32 (d, 1H, *J* = 5.8 Hz), 4.10 (dd, 1H, *J* = 5.8 Hz, *J* = 8.9 Hz), 3.63 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.5, 171.3, 140.8, 139.4, 137.4, 136.5, 130.3, 128.5, 128.3 X 2, 128.1 X 2, 128.0, 127.6, 126.5, 117.5, 70.7, 53.8, 52.1; Analytical data fits with literature.[6]

[6] Kanayama, T.; Yoshida, K.; Miyabe, H.; Kimachi, T.; Takemoto Y. *J. Org. Chem.* **2003,** 68, 6197-6201.



(2R,3R)-methyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate (10a')

To a 20 ml of 1% K_2CO_3 solution in methanol was added (2R,3R)-ethyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate **10a**, 50 mg (0.13 mmol), and after 1h of stiring at room temperature, methanol was removed and the crude rest was purified by flash column chromatography on silica gel (cyclohexane/Ethylacetate =15/1) to give the title compound (45 mg, 94%) as colourless oil.
$[\alpha]_D^{20}$ = + 175.5 (c = 1.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.50-7.11 (m, 13H), 6.73 (s, 2H), 5.96 (ddd, 2H, *J* = 8.9, *J* = 10.4, *J* = 17.4 Hz), 5.09 (d, 1H, *J* = 17.4 Hz), 5.02 (d, 1H, *J* = 10.4 Hz), 4.41 (d, 1H, *J* = 8.9 Hz), 4.10 (dd, 1H, *J* = 8.9, 8.9 Hz), 3.70 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.8, 171.3, 140.3, 139.7, 137.4, 135.9, 130.5, 128.9, 128.8 (2C), 128.3, 128.2, 128.1, 127.9, 126.8, 116.9, 71.4, 54.4, 52.3. Analytical data fits with literature.[6]



***tert*-butyl 2-cyano-3-phenylpent-4-enoate, (12a),**
(Table 4, Entry 1)
The general procedure C was followed with $[Ir(cod)Cl]_2$ (13 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), cinnamyl methylcarbonate (192 mg, 1 mmol), *t*-butyl cyanoacetate (155 mg, 1.1 mmol, 0.16 mL) and LiHMDS (184 mg, 1.1 mmol, 1.1 mL, 1.1 equiv.). The reaction was conducted at room temperature for 3h. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 65/35. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 18/1) to give the title compound (168 mg, 65 %) as yellow oil.
(Table 4, Entry 2)
The general procedure D was followed with $[Ir(cod)Cl]_2$ (13 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), cinnamyl methylcarbonate (192 mg, 1 mmol), t-butyl cyanoacetate (155 mg, 1.1 mmol, 0.16 mL 1.1 equiv.), KOH (62 mg, 1.1 mmol) and Bu_4NHSO_4 (16 mg, 0.2 mmol). The reaction was conducted at r.t. for 16 h. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 43/57. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 18/1) to give the title compound (160 mg, 62 %) as yellow oil.
(Table 4, Entry 3)
The general procedure D was followed with $[Ir(cod)Cl]_2$ (13 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), cinnamyl methyl carbonate (192 mg, 1 mmol), *t*-butyl cyanoacetate (155 mg, 1.1 mmol, 0.16 mL), NaOH (44mg, 1.1 mmol) and Bu_4NHSO_4 (16 mg, 0.2 mmol). The reaction was conducted at r.t. for 12 h. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 45/55. The crude reaction mixture

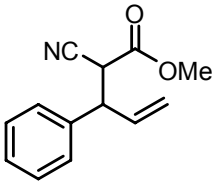
was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 18/1) to give the title compound (155 mg, 60 %) as yellow oil.

(Table 4, Entry 4)

The general procedure C was followed with $[Ir(cod)Cl]_2$ (13 mg, 0.02 mmol), ligand **2** (23 mg, 0.04 mmol), cinnamyl methylcarbonate (192 mg, 1 mmol), *t*-butyl cyanoacetate (155 mg, 1.1 mmol, 0.16 mL) and DABCO (23 mg, 0.2 mmol). The reaction was conducted at 50 °C for 18h. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 57/43. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 18/1) to give the title compound (196 mg, 76 %) as yellow oil.

(Table 4, Entry 5)

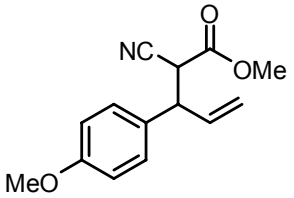
The general procedure B for allylic alkylations was followed with $[Ir(cod)Cl]_2$ (15 mg, 0.02 mmol), ligand **2** (19 mg, 0.04 mmol), cinnamyl methylcarbonate (192 mg, 1 mmol), and *t*-butyl cyanoacetate (155 mg, 1.1 mmol, 0.16 mL). The reaction mixture was stirred at r.t. for 5 days. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 52/48.The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexan/MTBE=9/1) to give to give the title compound (108 mg, 42 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39-7.26 (m, 10H), 6.21-6.04 (m, 2H), 5.27 (td, 4H, J = 16.72 Hz, J = 11.22 Hz, J = 11.22 Hz), 4.00 (dt, 2H, J = 7.60, J = 7.53, J = 2.79 Hz), 3.77 (d, 1H, J = 7.52 Hz), 3.71 (d, 1H, J = 7.16 Hz), 1.37 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 163.7 (C), 163.6 (C), 138.4 (C), 137.8 (C), 136.2 (CH), 135.0 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 119.0 (CH_2), 118.0 (CH_2), 115.7 (C), 115.7 (C), 84.2 (C), 84.1 (C), 49.9 (CH), 49.6 (CH), 27.6 (CH_3), 27.6 (CH_3); HRMS: m/z (HPLC-ESI) calc for $C_{16}H_{20}NO_2$ ($M+H^+$) 258.1489, found 258.1490; IR(film): ν [cm^{-1}] =3080 (m), 3021 (m), 2956 (s), 2240 (m), 1750 (vs), 1640 (m), 1615 (m), 1491 (m), 1435 (s), 1260 (s), 1124 (w), 1029 (m), 918 (s), 843 (w), 726 (m), 702 (m).



Methyl 2-cyano-3-phenylpent-4-enoate (mixture of diastereoisomers), (Table 5, Entry 1), (12b)

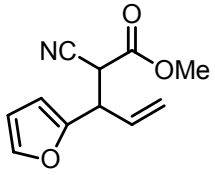
The general A procedure was followed with cinnamyl methylcarbonate (300 mg, 1.56 mmol, 1 equiv.), methylcyanoacetate (185 mg, 1.87 mmol, 1.2 equiv.), $[Ir(cod)Cl]_2$ (21 mg, 0.03 mmol, 0.02 equiv.), ligand **2** (35 mg, 0.06 mmol, 0.04 equiv.) and DABCO (35 mg, 0.31 mmol, 0.2 equiv.) in dry THF (4 mL). The reaction was conducted at 50 °C for 16 hours. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 50/50. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 5/1) to give the title compound (219 mg, 65 %) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38-7.28 (m, 5 H), 6.23-6.07 (m, 1 H), 5.34-5.24 (m, 2 H), 4.06 (dd, 1H, J = 8.0 Hz, J = 16.8 Hz), 3.89, 3.83 (2 d, 1H, J = 6.3 Hz, J = 7.4 Hz), 3.73 (s, 3H), 3.71 (s, 3 H); ^{13}C NMR (101 MHz, CDCl3) δ ppm 165.5 (2xC), 138.5, 137.7 (C), 136.0, 134.6 (CH), 129.1 (2xCH), 128.3, 128.1 (CH), 128.1, 127.7 (CH), 119.5,118.3 (CH2), 115.3 (2xC), 53.6, 53.5 (CH), 49.7 (2xCH3),

44.5, 44.0 (CH); HRMS: m/z (FAB) calc for $C_{13}H_{14}NO_2$ (M^+) 216.1025, found 216.1024; IR(film): ν [cm^{-1}] = 3086 (m), 3032 (s), 2956 (s), 2249 (m), 1755 (s), 1640 (m), 1602 (m), 1495 (m), 1435 (s), 1259 (s), 1124 (w), 1029 (m), 929 (s), 843 (w), 726 (m), 702 (m), 671 (w).



Methyl 2-cyano-3-(4-methoxyphenyl)pent-4-enoate (mixture of diastereomers), (Table 5, Entry 2), (12c)

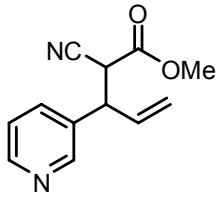
The general procedureA was followed with (*E*)-3-(4-methoxyphenyl)allyl methyl carbonate (300 mg, 1.35 mmol, 1 equiv.), cyanoacetate (160 mg, 1.62 mmol, 0.14 mL 1.2 equiv.), $[Ir(cod)Cl]_2$ (24 mg, 0.027 mmol, 0.02 equiv.), ligand **2** (31 mg, 0.054 mmol, 0.04 equiv.) and DABCO (30 mg, 0.27 mmol, 0.2 equiv.) in 4 mL dry THF. The reaction was conducted at 50 °C for 12 hours. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 50/50. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 5/1) to give the title compound (232 mg, 70 %) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.24-7.20 (m, 1H), 6.90-6.86 (m, 1H), 6.12 (dddd, 1H, *J* = 17.75 Hz, *J* = 17.16 Hz, *J* = 10.32 Hz, *J* = 7.88 Hz), 5.27 (td, 1H, *J* = 24.60 Hz, *J* = 12.53 Hz), 4.02 (dd, 1H, *J* = 14.22 Hz, *J* = 6.90 Hz), 3.87-3.84 (m, 1H), 3.79 (s, 1H), 3.78 (d, 1H ,*J* = 6.46 Hz), 3.72 (s, 1H), 3.71 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 165.4, 164.3 (C), 159.3, 159.2 (C), 136.1, 134.8 (CH), 130.3, 129.5 (C), 129.1, 128.7 (CH), 118.9, 117.7 (CH_2), 115.3, 115.2 (C), 114.3, 114.2 (CH), 55.2, 55.2 (CH_3), 53.3, 53.3 (CH_3), 48.9, 48.7 (CH), 45.0, 44.0 (CH). HRMS: m/z (EI) calc for $C_{14}H_{15}NO_3$ (M^+) 245.1046, found 245.1029; IR(film): ν [cm^{-1}] = 3461 (w), 3008 (m), 2955 (s), 2830 (s), 2364 (m), 2252 (m), 2068 (w), 1766 (vs), 1608 (vs), 1516 (s), 1431 (s), 1306 (m), 1273 (m), 1030 (s), 833 (s).



Methyl 2-cyano-3-(furan-2-yl)pent-4-enoate (mixture of diastereomers), (Table 5, Entry 3), (12d)

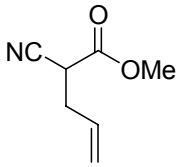
The general procedure A was followed with (*E*)-3-(furan-2-yl)allyl methyl carbonate (300 mg, 1.65 mmol, 1 equiv.), methylcyanoacetate (195 mg, 1.98 mmol, 1.2 equiv.), $[Ir(cod)Cl]_2$ (30 mg, 0.033 mmol, 0.02 equiv.), ligand **2** (38 mg, 0.066 mmol, 0.04 equiv.) and DABCO (37 mg, 0.33 mmol, 0.2 equiv.) in dry THF (4 mL). The reaction was conducted at 50 °C for 3 hours. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 55/45. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 5/1) to give the title compound (158 mg, 47 %) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38-7.40 (m, 2H), 6.36-6.33 (m, 2H), 6.28 (d, 1H, *J* = 3.21 Hz), 6.24 (d, 1H, *J* = 3.18 Hz), 6.11-5.97 (m, 2H), 5.35 (ddd, 4H, *J* = 14.26 Hz, *J* = 8.53 Hz, *J* = 4.96 Hz), 4.22-4.14 (m, 2H), 4.06 (d, 1H, *J* = 5.36 Hz), 3.88 (d, 1H, *J* = 6.35 Hz,), 3.80 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101

MHz, $CDCl_3$) δ ppm 165.0 (2xC), 151.0, 150.6 (C), 142.6, 142.5 (CH), 132.9, 131.6 (CH), 120.9, 119.7 (CH_2), 114.7, 114.6 (C), 110.6, 110.5 (CH), 107.9, 107.7 (CH), 53.5 ($2xCH_3$), 43.7, 43.6 (CH), 42.4, 42.3 (CH). HRMS: m/z (FAB) calc for $C_{11}H_{11}NO_3$ (M^+) 205.0739, found 205.0762; IR(film): ν [cm^{-1}] = 2962 (w), 2909 (m), 2850 (w), 2357 (w), 2245 (w), 1753 (vs), 1648 (w), 1503 (w), 1434 (m), 1267 (s), 1004 (m)938 (m).



Methyl 2-cyano-3-(pyridin-3-yl)pent-4-enoate (mixture of diastereomers), (Table 5, Entry 4), (12e)

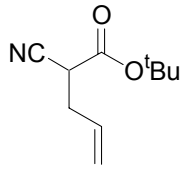
The general procedure A was followed with (*E*)-methyl 3-(pyridin-3-yl)allyl carbonate (200 mg, 1.04 mmol, 1 equiv.), cyanoacetate (112 mg, 1.14 mmol, 0.1 mL 1.1 equiv.), $[Ir(cod)Cl]_2$ (14 mg, 0.020 mmol, 0.02 equiv.), ligand **2** (24 mg, 0.042 mmol, 0.04 equiv.) and DABCO (23 mg, 0.207 mmol, 0.2 equiv.) in 2 mL dry THF. The reaction was conducted at 50 °C for 45 hours. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 50/50. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 1/2) to give the title compound (108 mg, 45 %) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58-8.54 (m, 3H), 8.52 (d, 1H, *J* = 1.61 Hz), 7.75-7.70 (m, 1H), 7.70-7.67 (m, 1H), 7.35-7.28 (m, 2H), 6.20-6.04 (m, 2H), 5.33 (ddd, 4H, *J* = 31.21 Hz, *J* = 16.46 Hz, *J* = 9.99 Hz), 4.14-4.09 (m, 2H), 3.93 (d, 1H, *J* = 6.62 Hz), 3.82 (d, 1H, *J* = 6.18 Hz), 3.75 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 164.8 (2xC), 149.6 (2xCH), 149.4, 149.2 (CH), 135.4, 135.0 (CH), 134.7 (CH), 134.0 (C), 133.4 (CH), 133.2 (C), 123.7 (2xCH), 120.4, 119.2 (CH_2), 114.7 (2xC), 53.7, 53.6 (CH_3), 46.9, 46.6 (CH), 43.9, 43.4 (CH); HRMS: m/z (EI) calc for $C_{12}H_{12}N_2O_2$ (M^+) 216.0893, found 216.0897; IR(film): ν [cm^{-1}] = 3474 (w), 3072 (m), 2962 (m), 2922 (w), 2259 (m), 1753 (vs), 1628 (m), 1582 (m), 1431 (s), 1247 (vs), 1194 (m), 1024 (m), 925 (s).



Methyl 2-cyanopent-4-enoate (Table 5, Entry 5), (12f)

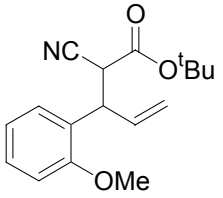
The general procedure A for allylic alkylations was followed with $[Ir(cod)Cl]_2$ (17 mg, 0.019 mmol), ligand **2** (19 mg, 0.033 mmol), DABCO (21 mg, 0.187 mmol), allyl methylcarbonate (85 mg, 0.723 mmol) and methylcyanoacetate (135 mg, 1.36 mmol). The reaction mixture was stirred at 50°C for 3 days The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexan/MTBE=9/1) to give 27 mg (0.194 mmol, 27% yield) of the title compound as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.81 (tdd, 1H, *J* = 17.1 Hz, *J* = 10.1 Hz, *J* = 7.01 Hz), 5.30-5.20 (m, 2H), 3.81 (s, 3H), 3.58 (dd, 1H *J* = 7.16 Hz, *J* =6.38 Hz), 2.74-2.63 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.0 (C), 131.2 (CH), 120.1 (CH_2), 116.0 (C), 53.5 (CH_3),

37.3 (CH), 33.8 (CH_2); HRMS: m/z (EI) calc for $C_7H_9NO_2$ (M^+) 139.0633, found 139.0615; IR(film): ν [cm^{-1}] = 3474 (w), 3072 (m), 2962 (m), 2922 (w), 2259 (m), 1753 (vs), 1635 (m), 1574 (m), 1432 m), 1242 (vs), 1194 (m), 1010 (m), 925 (s).



***tert*-butyl 2-cyanopent-4-enoate, (Table 5, Entry 6), (12g)**

The general procedure A was followed with $[Ir(cod)Cl]_2$ (25 mg, 0.037), ligand **2** (39 mg, 0.068 mmol,), DABCO (38 mg, 0.344 mmol) allylcarbonate (186 mg, 1.6 mmol) and t-butyl cyanoacetate (260 mg, 1.85 mmol), in dry THF (3 mL). The reaction was stirred at 50 °C for 48h. After standard workup crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 16:1) to give the title compound (138 mg, 47 %) as colourless oil. $[\alpha]_D^{20}$ = +0.9 (c = 0.937, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$). δ ppm 5.87-5.75 (m, 1H), 5.24 (t, 2H, *J* = 12.17 Hz), 3.46 (t, 1H, *J* = 6.72 Hz), 2.65 (t, 2H, *J* = 6.74Hz), 1.49 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 164.4 (C), 131.5 (CH), 119.8 (CH_2), 116.4 (C), 84.2 (C), 38.4 (CH), 33.9 (CH_2), 27.8 (3xCH_3).Analytical data fits with literature[7]

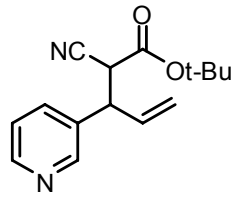


***tert*-butyl 2-cyano-3-(2-methoxyphenyl)pent-4-enoate, (Table 5, Entry 7), (12h)**

The general procedure A was followed with $[Ir(cod)Cl]_2$ (30 mg, 0.045 mmol, 0.02 equiv.), ligand **2** (49 mg, 0.09 mmol, 0.04 equiv.), DABCO (114 mg, 1.02 mmol, 0.45 equiv.), (*E*)-3-(2-methoxyphenyl)allyl methyl carbonate (500 mg, 2.25 mmol, 1 equiv.) and *t*-butyl cyanoacetate (349 mg, 2.47 mmol, 1.1 equiv.). The mixture was stirred at 50 °C for 20 hours. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 70/30. The crude reaction mixture was purified by flash column chromatography using cyclohexane/MTBE (10:1) as eluent to afford title compound (407 mg, 70% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30-7.21 (m, 4H), 6.98-6.84 (m, 2H), 6.29-6.07 (m, 2H), 5.30 (dd, 1H, *J* = 13.61 Hz, *J* = 7.31 Hz), 5.20 (dd, 1H, *J* = 13.49 Hz, *J* = 9.31 Hz), 4.32-4.22 (m, 1H), 4.05 (dd, 1H, *J* = 14.97 Hz, *J* = 8.10 Hz), 3.86 (s,3H), 3.85 (s,3H), 1.40 (s, 9H),1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 164.2, 164.1 (C), 156.8, 156.5 (C), 135.3, 134.2 (CH), 129.2 (2xCH), 129.0, 128.9 (2xCH), 120.8 (2xCH), 118.9, 118.1 (2xCH_2), 116.2, 116.1 (C), 110.9, 110.6 (2xCH), 83.7, 83.6 (C), 55.3 (2xCH_3), 45.8, 45.5 (2xCH), 42.8, 42.7 (2xCH), 27.6 (6xCH_3). HRMS: m/z (ESI) calc for $C_{17}H_{21}NO_3$ ($M+H^+$) 287.15214, found 287.15221;

[7] Wang, X. S.; Kitamura, M.; Maruoka, K.. *J. Am. Chem. Soc.* **2007,** 129, 1038-1039.

IR(film): ν [cm^{-1}] = 3474 (w), 3073 (m), 2981 (s), 2935 (m), 2239 (m), 1740 (vs), 1589 (s), 1490 (s), 1450 (s), 1234 /s), 1135 (vs), 1017 (s), 938 (s), 835 (s).

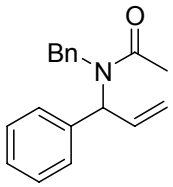


***tert*-butyl 2-cyano-3-(pyridin-3-yl)pent-4-enoate (mixture of diastereomers), (Table 5, Entry 8), (12i)**

The general procedure A was followed with (*E*)-methyl 3-(pyridin-3-yl)allyl carbonate (200 mg, 1.04 mmol, 1 equiv.), *t*-butyl cyanoacetate (175 mg, 1.24 mmol, 0.18 mL 1.2 equiv.), $[Ir(cod)Cl]_2$ (14 mg, 0.020 mmol, 0.02 equiv.), ligand **2** (23 mg, 0.04 mmol, 0.04 equiv.) and DABCO (23 mg, 0.207 mmol, 0.2 equiv.) in 1 mL dry THF. The reaction was conducted at 50 °C for 48 hours. 1H-NMR of the crude reaction mixture indicated the ratio of diastereoisomers to be 52/48. The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 3/2) to give the title compound (133 mg, 60 %) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58-8.53 (m, 1H), 7.78-7.74 (m, 1H), 7.68-7.65 (m, 1H), 7.31 (td, 1H, *J* = 7.95 Hz, *J* =5.05 Hz, *J* =5.05 Hz), 6.17-6.05 (m, 1H), 5.37 (d, 1H, *J* = 10.30 Hz), 5.35-5.24 (m, 1H), 4.06 (dt, 1H, *J* = 7.51 Hz, *J* = 7.21 Hz, *J* = 3.73 Hz), 3.81 (d, 1H, *J* = 6.73 Hz), 3.70 (d, 1H, *J* = 6.97 Hz), 1.38 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 163.2 (2xC), 149.8 (CH), 149.4 (2xCH), 149.2 (CH), 135.4, 135.1 (CH), 135.1 (CH), 134.1 (C), 133.8 (CH), 133.4 (C), 123.5 (2xCH), 119.9, 118.9 (CH_2), 115.2 (2xC), 84.7, 84,6 (C), 47.1, 46.6 (CH), 44.6, 44.2 (CH), 27.5 (6x CH_3); HRMS: m/z (HPLC-ESI) calc for $C_{15}H_{19}N_2O_2$ ($M+H^+$) 259.1441, found 259.1441; IR(film): ν [cm^{-1}] = 3435 (w), 2988 (s), 2929 (m), 2252 (m), 2200 (m), 1864 (w), 1740 (vs), 1648 (w), 1569 (m), 1483 (s), 1424 (s), 1378 (s), 1268 (s), 1142 (s), 918 (s).

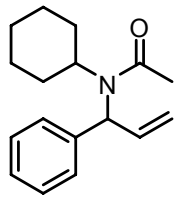
General Procedure for Acetylation of the Secondary Amines:

To a stirred solution of amine (1 equiv.) in 10 ml of dry CH_2Cl_2 was added DMAP (0.05 equiv.) and dry triethylamine (3 equiv.) and the mixture was degassed under argon atmosphere using an ultrasound bath. Reaction mixture was cooled down to 0 °C and acetylchloride (2 equiv.) was added dropwise via syringe. The mixture was allowed to stir at room temperature until amine was fully converted as determined by TLC. After completion of the reaction solvent was evaporated and 10 ml of diethylether were added. The formed suspension was filtered through sintered glass filter, and the volatiles removed *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate or cyclohexane/MTBE) to give the desired product.



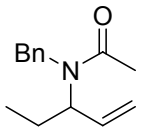
***N*-benzyl-*N*-(1-phenylallyl)acetamide**

(Table 6, Entry 1), (14a), (R-(-)). The general procedure was followed with *N*-benzyl-1-phenylprop-2-en-1-amine (447 mg, 2.0 mmol), DMAP (12 mg, 0.1 mmol), triethylamine (607 mg, 0.79 ml, 6.0 mmol) and acetylchloride (314 mg, 0.285 ml, 4.0 mmol) in 10 ml of CH_2Cl_2. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (467 mg, 88 %) as viscous colourless oil. $[\alpha]_D^{20}$ = -44.6 (c = 1.60, $CHCl_3$); **(Table 6, Entry 2), (14a),** (S-(+)). The general procedure was followed with *N*-benzyl-1-phenylprop-2-en-1-amine (447 mg, 2.0 mmol), DMAP (12 mg, 0.1 mmol), triethylamine (607 mg, 0.79 ml, 6.0 mmol) and acetylchloride (314 mg, 0.285 ml, 4.0 mmol) in 10 ml of CH_2Cl_2. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (452 mg, 85 %) as viscous colourless oil.
$[\alpha]_D^{20}$ =+46.2 (c = 1.12, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.37-7.18 (m, 8 H), 7.05 (d, 2 H, *J* = 7.0 Hz), 6.48,5.54, (2d, 1 H, *J* = 4.6 Hz, *J* = 6.8 Hz), 6.01 (ddd, 1H, *J* = 6.9 Hz, *J* = 10.3 Hz, *J* = 17.3 Hz), 5.33-5.11 (m, 2 H), 4.75-4.35 (m, 2 H), 2.23, 2.07 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.8 (s, C), 139.2 (s, C), 137.9 (s, C), 135.2, 135.0 (d, CH), 128.7, 128.6, 128.1, 127.9, 127.7, 127.6, 127.1, 126.7, 126.1 (10d, CH), 119.2, 118.8 (t, CH2), 64.7, 60.1 (d, CH), 49.4, 47.5 (t, CH2), 22.6, 22.5,(q, CH3); HRMS: m/z (ESI) calc for $C_{18}H_{20}NO$ ($M+H^+$) 266.15394, found 266.15400; IR(film): ν [cm^{-1}] = 3060 (m), 3021 (m), 2929 (m), 1943 (w), 1818 (w), 1648 (vs), 1497 (s), 1418 (vs), 1260 (m), 1188 (m), 918 (m).



***N*-cyclohexyl-N-(1-phenylallyl)acetamide (Table 6, Entry 3), (14b)**

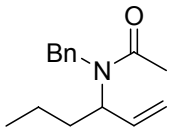
The general procedure was followed with *N*-(1-phenylallyl)cyclohexanamine (193mg, 0.896mmol), DMAP (5 mg, 0.041 mmol), triethylamine (145 mg, 2.79 mmol) and acetylchloride (145 mg, 1.86 mmol) in 10 ml of CH_2Cl_2. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 2/1) to give the title compound (213 mg, 92 %) as viscous yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.14 (m, 10H), 6.62-6.45 (m, 1H), 6.34-6.14 (m, 1H), 5.44 (d, 1H, *J* = 10.05 Hz), 5.39-5.15 (m, 4H), 5.03 (bs, 1H), 4.10 (bs, 1H), 3.61 (t, 1H, *J* = 11.1 Hz,), 2.17 (s, 1H), 1.99-1.44 (m, 18H), 1.86 (s, 3H), 1.68 (s, 3H), 1.40-1.00 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$). δ ppm 171.1, 169.3, 140.5, 140.1, 137.5, 136.1, 128.4, 127.9, 127.2, 126.8, 126.5, 126.3, 118.7, 117.3, 60.9, 60.6, 59.2, 55.3, 32.5, 32.0, 31.0, 30.4, 26.1, 26.0, 24.7, 23.4; HRMS: m/z (FAB) calc for $C_{17}H_{23}NO$ (M^+) 257.1780, found 257.1787; IR(film): ν [cm^{-1}] = 3028 (w), 2929 (s), 2853 (s), 1644 (s), 1449 (s), 1427 (s), 699 (s);



***N*-Benzyl-*N*-(1-ethyl-allyl)-acetamide (Table 6, Entry 4), (14c)**

The general procedure was followed with *N*-benzylpent-1-en-3-amine (315 mg, 1.80 mmol), DMAP (11 mg, 0.089 mmol), triethylamine (547 mg, 0.72 ml, 5.4 mmol) and acetylchloride (283 mg, 0.26 ml, 3.6 mmol) in 10 ml of CH_2Cl_2. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (293 mg, 75 %) as viscous colourless oil.

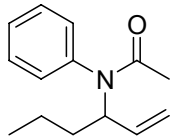
$[\alpha]_D^{20}$ = -48.7 (c = 1.634 $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.30 (t, 1H, *J* = 7.3 Hz), 7.26-7.15 (m, 4H), 5.73 (dddd, 1H, *J* = 6.4 Hz, *J* = 10.4 Hz, *J* = 16.7 Hz, *J* = 23.4 Hz), 5.17-5.06 (m, 2H), 4.95 (dd, 1H, *J* = 7.1 Hz, *J* = 14.3 Hz), 4.68 (d, 1H, *J* = 15.4 Hz), 4.43 (s, 1H), 4.31 (d, 1H, *J* = 15.4 Hz), 4.12 (dd, 1H, *J* = 6.6 Hz, *J* = 12.9 Hz), 2.20, 2.00 (s, 3H), 1.58 (p, 2H, *J* = 7.3 Hz), 0.81 (dt, 3H, *J* = 7.3 Hz, *J* = 24.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.6, 139.2, 138.1, 136.6, 136.4, 128.6, 128.1, 127.6, 127.1, 126.6, 126.1, 117.6, 116.6, 62.8, 58.3, 48.4, 45.4, 25.6, 24.6, 22.5, 22.3, 11.0, 10.9; HRMS: m/z (FAB) calc for $C_{14}H_{20}NO$ (M^+) 218.15394, found 218.15381; IR(film): ν [cm^{-1}] = 2968 (s), 2929 (m), 2876 (m), 1753 (m), 1641 (vs), 1457 (s), 1411 (s), 1254 (w), 1208 (m), 925 (s), 728 (s).



_N_-benzyl-_N_-(hex-1-en-3-yl)acetamide (Table 6, Entry 5), (14d)

The general procedure was followed with *N*-benzylhex-1-en-3-amine (294 mg, 1.55 mmol), DMAP (9.5 mg, 0.078 mmol), triethylamine (471 mg, 0.62 ml, 4.65 mmol) and acetylchloride (243 mg, 0.22 ml, 3.10 mmol) in 10 ml of CH_2Cl_2. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (280 mg, 78 %) as colourless oil.

$[\alpha]_D^{20}$ = -41.5 (c = 0.836, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.33 (t, 2H, *J* = 7.5 Hz), 7.26 (d, 2H, *J* = 7.9Hz), 7.20 (d, 1H, *J* = 7.9 Hz), 5.73 (dddd, 1H, *J* = 6.3 Hz, *J* = 10.4 Hz, *J* = 16.8 Hz, *J* = 27.6 Hz), 5.18-5.01 (m, 2.5H), 4.72 (d, 0.5 H, *J* = 15.4 Hz), 4.43 (d, 1H, *J* = 1.7 Hz), 4.28 (d, 0.5H, *J* = 15.4 Hz), 4.24-4.20 (m, 0.5H), 2.20, 2.00 (s, 3H),1.58-1.50 (m, 2H), 1.32-1.12 (m, 2H), 0.84, 0.73 (t, 1H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 171.6 (s, C), 139.2,138.1 (s, C), 136.9, 136.7 (d, CH), 128.6, 128.2, 127.6, 127.1, 126.7, 126.1 (6d, CH), 117.4, 116.5 (t, CH_2), 60.9, 56.6 (d, CH), 48.5, 45.5 (t, CH_2), 34.6, 33.7 (t, CH_2), 22.5, 22.3 (q, CH_3), 19.6 (t, CH_2), 13.9, 13.6 (q, CH_3); HRMS: m/z (ESI) calc for $C_{15}H_{22}NO$ ($M+H^+$) 232.16959, found 232.16945; IR(film): ν [cm^{-1}] = 2955 (s), 2922 (s), 2870 (m), 1955 (w), 1648 (vs), 1420 (m), 1200 (w), 978 (m).



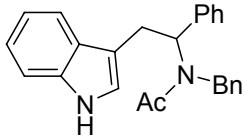
_N_-Phenyl-_N_-(1-propyl-allyl)-acetamide (Table 6, Entry 6), (14e)

The general procedure was followed with *N*-(hex-1-en-3-yl)aniline (203 mg, 1.16 mmol), DMAP (7 mg, 0.058 mmol), triethylamine (352 mg, 0.46 ml, 3.48 mmol) and acetylchloride (180 mg, 0.163 ml, 2.30 mmol) in 10 ml of CH_2Cl_2. The crude reaction

mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 4/1) to give the title compound (192 mg, 76 %) as viscous colourless oil.
$[\alpha]_D^{20}$ = -12.7 (c = 0.937, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.30 (m, 3H), 7.08 (d, *J* = 6.82 Hz, 2H), 5.66-5.52 (m, 1H), 5.22-5.12 (m, 2H), 5.08 (d, *J* = 10.26 Hz, 1H), 1.73 (s, 3H), 1.57-1.42 (m, 1H), 1.41-1.27 (m, 3H), 0.88 (t, *J* = 7.00 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.0 (C), 139.9 (C), 137.2 (CH), 129.9 (CH), 129.1 (CH), 128.0 (CH), 117.4 (CH_2), 57.3 (CH), 34.2 (CH_2), 23.3 (CH_3), 19.5 (CH_2), 13.8 (CH_3); HRMS: m/z (ESI) calc for $C_{14}H_{20}NO$ ($M+H^+$) 218.15394, found 218.15381; IR(film): ν [cm^{-1}] = 3063 (w), 2958 (s), 2931 (s), 2872 (s), 1660 (s), 1594 (s), 1494 (s), 1382 (s), 1313 (s), 702 (s);

General procedure for hydroformylation/Fischer indole synthesis with subsequent addition of bronsted acid (general method A)
In a thick walled sample vial containing PTFE septum $Rh(acac)(CO)_2$ (0.01 equiv.), XANTPHOS (0.1 equiv.), phenylhydrazine (1 equiv.) and olefin (1 equiv.) were dissolved in dry THF (5 mL). The vial was placed in a pressure vessel, flushed with argon and pressurized with 10 bar H_2 and 10 bar CO. The reaction mixture was stirred for 5 days at 80 °C. A 4 wt. % solution of H_2SO_4 in THF (5 mL) was slowly added and the resulting mixture was refluxed for 3 hours. Reaction was quenched with ammonia solution (30% in water) and the aqueous phase was extracted with 4x10 mL DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate or cyclohexane/MTBE) to give the desired product.

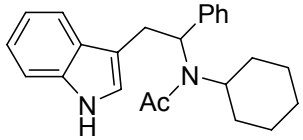
General procedure for hydroformylation/ Fischer indole synthesis with subsequent addition of Lewis acid (general method B)
In a thick walled sample vial containing PTFE septum olefin (1 equiv.), phenylhydrazine (1 equiv.), $Rh(acac)(CO)_2$ (0.01 equiv.) and XANTPHOS (0.1 equiv.) were dissolved in dry THF (5 mL). The vial was placed in a pressure vessel, flushed with argon and pressurized with 10 bar H_2 and 10 bar CO. The reaction mixture was stirred for 5 days at 80 °C. After completion of the reaction volatiles were removed in vacuo, residue was dissolved in toluol (10 mL) and $ZnCl_2$ (4 eq) was added and the resulting mixture was refluxed for 12 hours. Reaction mixture was diluted with water and the aqueous phase was extracted with 4x10 mL DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethylacetate or cyclohexane/MTBE) to give the desired product.



***N*-Benzyl-*N*-[2-(1H-indol-3-yl)-1-phenyl-ethyl]-acetamide**
(Table 7, Entry 1), (15a), (R-(+)) The general procedure A was followed with *N*-benzyl-*N*-(1-phenyl-allyl)-acetamide (335 mg, 1.26 mmol), phenylhydrazine (136 mg, 1.26

mmol), $Rh(acac)(CO)_2$ (4.5 mg, 0.013 mmol) and XANTPHOS (73 mg, 0.13 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (288 mg, 62 % yield) of the title compound as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 92 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 90/10; flow rate = 2 ml/min; detection wavelength = 254 nm; TR = 11.3 (+), 14.2 (-) min]. $[\alpha]_D^{20}$ = + 2.1 (*c* = 1.800, $CHCl_3$);

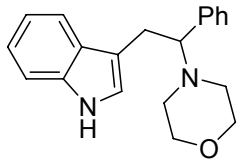
(Table 7, Entry 2), (15a), (S-(-)) The general procedure A was followed with *N*-benzyl-*N*-(1-phenyl-allyl)-acetamide (265 mg, 1.0 mmol), phenylhydrazine (109 mg, 1.26 mmol), $Rh(acac)(CO)_2$ (4 mg, 0.01 mmol) and XANTPHOS (60 mg, 0.1 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (240 mg, 65 % yield) of the title compound as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 97 % [Diacel Chiralcel AD (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 90/10; flow rate = 2 ml/min; detection wavelength = 254 nm; TR = 11.2 (+), 14.3 (-) min]. $[\alpha]_D^{20}$ = - 2.0 (*c* = 1.800, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.25, 8.16 (2 bs, 1 H, NH) , 7.85-7.07 (m, 13 H, 13 x CH), 6.91 (d, 1 H, *J* = 4.5 Hz, CH), 6.97, 6.47 (2 s, 1 H, CH), 6.36, 5.38 (dd, *t*, 1H, *J* = 4.9 Hz, *J* = 9.3 Hz, *J* = 7.8 Hz, CH), 4.45, 4.29 (2 d, 1 H, *J* = 17.6 Hz, CH*H*), 4.73, 4.21 (2 d, 1 H, *J* = 15.0 Hz, *J* = 14.9 Hz, C*H*H), 3.48-3.31 (m, 2 H, CH2), 2.02, 1.82, (2 s, 3 H, CH3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 172.1 (s, C), 142.4 (s, C), 139.9 (s, C), 137.9 (s, C), 131.8, 131.7, 128.8, 128.6, 128.5, 128.1, 127.7, 127.4 (2 d, CH), 127.3, 127.1, 126.8, 126.3 (s, C), 122.6, 122.2, 122.0, 119.7, 119.4, 118.8, 118.1 (2 d, CH), 112.5 (s, C), 111.6, 111.1 (2 d, CH), 62.0, 57.1 (2 d, CH), 49.0, 45.9 (2 t, CH2), 27.8, 27.1 (2 t, CH2), 23.0, 22.2 (2 q, CH3); HRMS: m/z (FAB) calc for $C_{25}H_{25}N_2O$ ($M+H^+$) 369.1967, found 369.2004; IR(film): ν [cm^{-1}] = 3419 (w), 3273 (m), 3029 (w), 2925 (w), 1630 (s), 1495 (m), 1455 (m), 1421 (m), 1360 (w), 1336 (w), 1028 (w), 981 (w), 743 (s), 699 (s), 542 (w);



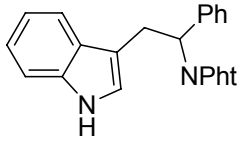
***N*-(2-(1H-indol-3-yl)-1-phenylethyl)-*N*-cyclohexylacetamide, (Table 7, Entry 3), (15b)**

The general procedure A was followed with *N*-cyclohexyl-*N*-(1-phenylallyl)acetamide (100 mg, 0.39 mmol), phenylhydrazine (42 mg, 0.39 mmol), $Rh(acac)(CO)_2$ (1 mg, 0.004 mmol) and XANTPHOS (22 mg, 0.038 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 1/2) to give (64 mg, 45 % yield) of the title compound as yellow oil. $[\alpha]_D^{20}$ = +46.4 (c = 0.507, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.49 (s, 1H), 8.23 (s, 1H), 7.71 (d, 1H, *J* = 7.36 Hz), 7.58 (d, 1H, *J* = 7.73 Hz), 7.49 (d, 2H, *J* = 7.43 Hz), 7.44 (d, 2H, *J* = 7.29 Hz), 7.41-7.24 (m, 8H), 7.24-7.09 (m, 4H), 6.94 (d, 2H, *J* = 23.79 Hz), 5.20 (dd, 1H, *J* = 7.79 Hz, *J* = 5.35 Hz), 3.81 (dd, 1H, *J* = 11.52 Hz, *J* = 6.95 Hz), 3.70-3.54 (m, 2H), 3.31 (dd, 2H, *J* = 14.79 Hz, *J* = 8.77 Hz), 2.18 (s, 3H), 1.78 (s, 3H), 1.70-1.43 (m, 10H), 1.41-1.00 (m, 6H), 1.00-0.70 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.9, 170.8 (2xC), 139.8

(2xC), 136.1 (2xC), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.2 (C), 126.6 (CH), 123.0, 122.9 (2xCH), 122.0 (CH), 121.6 (CH), 119.4 (CH), 119.1 (CH), 118.5 (CH), 118.0 (CH), 111.6 (C), 111.5 (CH), 111.2 (CH), 56.6 (CH),32.2 (CH_2), 30.4 (CH_2), 29.2 (CH_2), 26.7 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 25.3 (CH_2), 25.2 (CH_2), 24.2 (CH_3), 23.9 (CH_3); HRMS: m/z (HPLC-ESI) calc for $C_{24}H_{29}N_2O$ ($M+H^+$) 361.2274, found 361.2268; IR(film): ν [cm^{-1}] = 3279 (s), 3058 (s), 2930 (s), 2853 (s), 1719 (m), 1633 (s), 1494 (s), 1454 (s), 1380 (s), 1366 (s), 1316 (s), 909 (s), 738 (s), 699 (s), 646 (m);

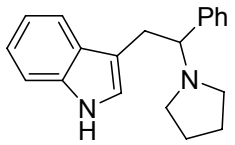


4-(2-(1H-indol-3-yl)-1-phenylethyl)morpholine, (Table 7, Entry 4), (15c)
The general procedure A was followed with 4-(1-phenylallyl)morpholine (150 mg, 0.738 mmol), phenylhydrazine (80 mg, 0.738 mmol), $Rh(acac)(CO)_2$ (1.92 mg, 0.007 mmol) and XANTPHOS (43 mg, 0.07 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (119 mg, 52 % yield) of the title compound as yellowish oil. HPLC analysis indicated that the enantiomeric excess of the product was 97 % [Diacel Chiralcel OD (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 95/5; flow rate = 2 ml/min; detection wavelength = 254 nm; TR = 16.2 (+), 18.2 (-) min]. $[\alpha]_D^{20}$ = -41.6 (c = 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (bs, 1H), 7.55 (d, 1H, *J* = 7.9 Hz), 7.14-7.34 (m, 7H), 7.10 (t, 1H, *J* = 7.4 Hz), 6.56 (d, 1H, *J* = 2.5 Hz), 3.74 (t, 4H, *J* = 4.6 Hz,), 3.64 (dd, 1H, *J* = 4.8 Hz, *J* = 9.6 Hz), 2.51-2.55 (m, 2H), 3.50 (dd, 1H, *J* = 4.5 Hz, *J* = 14.4 Hz), 3.08 (dd,1H , *J* = 9.6 Hz, *J* = 14.3 Hz,), 2.61-2.66 (m, 2H); ^{13}C NMR (CDCl3, 101 MHz) δ 140.8 (C). 136.0 (C), 128.9 (CH), 128.0 (CH), 127.8 (C), 127.1 (CH), 122.7 (CH), 121.8 (CH), 119.2 (CH), 118.7 (CH), 113.2 (C), 111.1 (CH), 71.0 (CH), 67.5 (CH2), 51.5 (CH2), 28.6 (CH2); HRMS: m/z (FAB) calc for $C_{20}H_{23}N_2O$ ($M+H^+$) 307.1810, found 307.1805; IR(film): ν [cm^{-1}] = 3396 (m), 3012 (m), 3027 (w), 2954 (s), 2853 (s), 2810 (s), 1599 (s), 1500 (s), 1452 (s), 1272 (m), 1116 (s), 1068 (m), 876 (m), 742 (s), 703 (s).

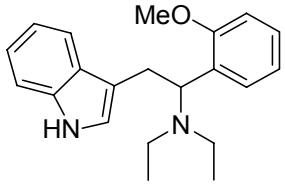


2-(2-(1H-indol-3-yl)-1-phenylethyl)isoindoline-1,3-dione, (Table 7, Entry 5), (15d)
The general procedure A was followed with phthalimide (300 mg, 2 mmol), phenylhydrazine (220 mg, 2 mmol), $Rh(acac)(CO)_2$ (5.2 mg, 0.02 mmol) and XANTPHOS (120 mg, 0.2 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (Cyclohexane/EtOAc/ = 2/1) to give (491 mg, 67 % yield) of the title compound as yellowish oil. $[\alpha]_D^{20}$ = +112.5 (c = 0.810, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.05 (s, 1H), 7.72-7.63 (m, 4H), 7.54 (dd, 2H, *J* = 3.1 Hz, *J* = 5.3 Hz), 7.37 (t, 2H, *J* = 7.4 Hz), 7.31 (d, 1H, *J* = 7.2 Hz), 7.23 (d, 1H, *J* = 7.1 Hz), 7.16-7.08 (m, 2H), 6.92 (s, 1H), 5.85 (dd, 1H, *J* = 6.0 Hz, *J* = 10.4 Hz), 4.19 (dd, 1H, *J* = 10.5 Hz, *J* = 14.9 Hz), 3.70 (dd, 1H, *J* = 6.0 Hz, *J* = 14.9 Hz); ^{13}C-NMR ($CDCl_3$,

100 MHz) δ ppm 168.3, 139.6, 136.0, 133.7, 131.6, 128.5, 128.0, 127.8, 127.2, 122.9, 122.4, 121.8, 119.3, 118.5, 112.0, 111.0, 54.9, 27.1; HRMS: m/z (ESI) calc for $C_{24}H_{19}N_2O_2$ ($M+H^+$) 367.1410, found 367.14410; IR(film): ν [cm^{-1}] = 3441 (w), 3054 (w), 2929 (w), 1757 (w), 1707 (vs), 1615 (m), 1398 (s), 1352 (s), 1319 (m), 1102 (m), 715 (s).

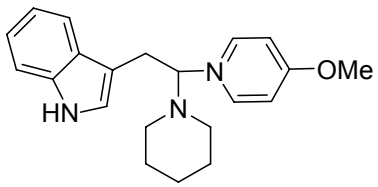


3-(2-phenyl-2-(pyrrolidin-1-yl)ethyl)-1H-indole, (Table 7, Entry 6), (15e)
The general procedure A was followed with 1-(1-phenylallyl)pyrrolidine (100 mg, 0.533 mmol), phenylhydrazine (58 mg, 0.533 mmol), $Rh(acac)(CO)_2$ (1.55 mg, 0.006 mmol) and XANTPHOS (36 mg, 0.062 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (73 mg, 47 % yield) of the title compound as brown oil. HPLC analysis indicated that the enantiomeric excess of the product was 98 % [Diacel Chiralcel OD (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 95/5; flow rate = 2 ml/min; detection wavelength = 254 nm; TR = 7.1 (-), 9.2 (+) min]. $[\alpha]_D^{20}$ = -112.9 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.98 (bs, 1H), 7.54 (d, 1H, *J* = 7.9 Hz), 7.27 (d, 1H, *J* = 7.8 Hz) , 7.07-7.21 (m, 6 H), 6.40 (d, 1H, *J* = 2.1 Hz), 4.48 (dd, *J* = 3.9 Hz, *J* = 10.4 Hz, 1 H), 3.58 (dd, *J* = 3.6 Hz, *J* = 13.8 Hz, 1 H), 3.11 (dd, 1H, *J* = 10.5 Hz, *J* = 14.0 Hz,), 2.77-2.79 (m, 2 H), 2.54-2.57 (m, 2 H), 1.79-1.85 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 143.1 (s, C), 136.0 (s, C), 128.5 (2 d, CH), 128.0 (2 d, CH), 127.8 (s, C), 127.1 (d, CH), 122.9 (d, CH), 121.7 (d, CH), 119.2 (d, CH), 118.9 (d, CH), 112.9 (s, C), 111.0 (d, CH), 71.8 (d, CH), 53.3 (2 t, CH2), 32.0 (t, CH2), 23.4 (2 t, CH2); HRMS: m/z (FAB) calc for $C_{20}H_{23}N_2$ ($M+H^+$) 291.1861, found 291.1846; IR(film): ν [cm^{-1}] = 3478 (m), 3424 (m), 2969 (m), 2794 (m), 1731 (m), 1492 (m), 1455 (s), 1372 (m), 1046 (m), 915 (w), 889 (w), 702 (s).

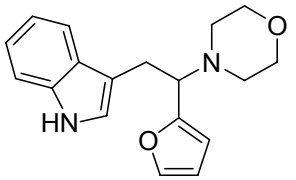


***N,N*-diethyl-2-(1H-indol-3-yl)-1-(2-methoxyphenyl)ethanamine, (Table 7, Entry 7), (15f)**
The general procedure A was followed with *N,N*-diethyl-1-(2-methoxyphenyl)prop-2-en-1-amine (150 mg, 0.68 mmol), phenyl hydrazine (74 mg, 0.68 mmol), $Rh(acac)(CO)_2$ (1.78 mg, 0.0068 mmol) and XANTPHOS (40 mg, 0.068 mmol, 0.1 equiv.). The crude reaction mixture was purified by column chromatography on silica gel (DCM/MeOH/triethylamine = 10/1/0.1) to give (74 mg, 33 % yield) of the title compound as brown solid. $[\alpha]_D^{20}$ = -20.45 (c = 1.700, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm, 7.79 (bs, 1H), 7.61 (d, 1H, *J* = 7.66 Hz), 7.45 (d, 1H, *J* = 7.33 Hz), 7.25 (d, 1H, *J* = 6.49 Hz), 7.19-7.03 (m, 1H), 6.92 (t, 1H, *J* = 7.41Hz), 6.74 (d, 1H, *J* = 8.13 Hz), 6.67 (s, 1H), 4.77 (dd, 1H, *J* = 9.52 Hz, *J* = 5.33 Hz), 3.48 (s, 1H), 3.38 (dd, 1H, *J* =

14.52 Hz, *J* = 5.19 Hz), 3.14 (dd, 1H, *J* = 14.47 Hz, *J* = 9.65 Hz), 2.79 (qd, 1H, *J* = 14.18, *J* = 7.14 Hz, *J* = 7.13 Hz), 2.50 (qd, 1H, *J* = 13.49 Hz, *J* = 6.79 Hz, *J* = 6.79 Hz), 1.06 (t, 1H, *J* = 7.05 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 158.1 (C), 135.8 (C), 128.5 (CH), 128.0 (CH), 127.4 (CH), 122.1 (CH), 121.4 (CH), 120.1 (CH), 118.8 (2xCH), 114.0 (C) 110.7 (2xCH), 55.8 (CH), 55.3 (CH_3), 43.4 (CH_2), 28.5 (CH_2), 12.8 (CH_3); HRMS: m/z (FAB) calc for $C_{21}H_{26}N_2O$ ($M+H^+$) 322.2045, found 323.2098; IR(film): ν [cm^{-1}] = 3450 (s), 2975 (s), 1615 (s), 1510 (s), 1410 (s), 1255 (s), 1178 (s), 1035 (s), 747 (s);

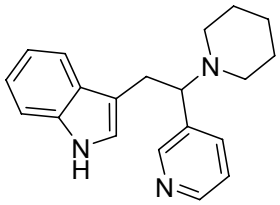


3-(2-(4-methoxyphenyl)-2-(piperidin-1-yl)ethyl)-1H-indole, (Table 7, Entry 8), (15g)
The general procedure A was followed with *N*-1-(1-(4-Methoxyphenyl) allyl) piperidin (150 mg, 0.64 mmol), Phenylhydrazin (70 mg, 0.64 mmol), Rh(acac)(CO)2 (1.71 mg, 0.006 mmol) and XANTPHOS (37 mg, 0.06 mmol). The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 1/1) to give (116 mg, 50 % yield) of the title compound as white solid. $[\alpha]_D^{20}$ = -25.45 (c = 1.700, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.81 (bs, 1H), 7.60 (d, 1H, *J* = 7.61 Hz), 7.32-7.24 (m, 1H), 7.18-7.05 (m, 4H), 6.79 (d, 2H, *J* = 8.43 Hz), 6.62 (s, 1H), 3.77 (s, 3H), 3.77-3.75 (m, 1H), 3.46 (dd, 1H, *J* = 15.34, *J* = 5.16 Hz), 3.24-3.14 (m, 1H), 2.50 (bs, 4H), 1.61 (bs, 4H), 1.39 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 159.2 (C), 135.8 (C), 129.8 (2xCH), 129.8 (C), 128.0 (CH), 127.7 (C), 122.5 (CH), 121.3 (CH), 118.7 (CH), 113.4 (C), 112.9 (2xCH), 110.9 (CH), 69.9 (CH), 55.5 (CH3), 51.3 (CH2), 29.6 (CH2), 28.2 (CH2), 26.3 (2xCH2), 24.6 (CH2); HRMS: m/z (ESI) calc for $C_{22}H_{27}N_2O$ ($M+H^+$) 335.2118, found 335.2118; IR(KBr): ν [cm^{-1}] = 3444 (s), 2956 (s), 1609 (s), 1515 (s), 1457 (s), 1403 (s), 1255 (s), 1181 (s), 1027 (s), 747 (s);

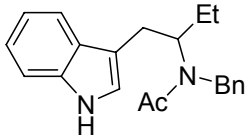


3-(2-Furan-2-yl-2-morpholin-4-yl-ethyl)-1H-indole, (Table 7, Entry 9), (15h)
The general procedure A was followed with 4-(1-furan-2-yl-allyl)-morpholine (315 mg, 1.63 mmol), phenylhydrazine (176 mg, 1.63 mmol), $Rh(acac)(CO)_2$ (5.8 mg, 0.016 mmol) and XANTPHOS (94 mg, 0.16 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (270 mg, 56 % yield) of the title compound as brown oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 7.98 (s, 1H), 7.56 (d, 1H, *J* = 7.8 Hz), 7.37 (s, 1H), 7.28 (d, 1H, *J* = 8.0 Hz), 7.12 (dt, 2H, *J* = 7.2 Hz, *J* = 25.3 Hz), 6.76 (s, 1H), 6.24 (dd, 1H, *J* = 2.0 Hz, *J* = 2.7 Hz), 6.04 (d, 1H, *J* = 3.1 Hz), 3.85 (t, 1H, *J* = 7.4 Hz), 3.73 (m, 4H), 3.31 (d, 2H, *J* = 7.4 Hz), 2.57 (dtd, 2H, *J* = 4.9 Hz, *J* = 10.9 Hz, *J* = 15.6 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 153.6, 141.7, 136.0, 127.7, 122.4, 121.9, 119.3, 118.7, 113.1, 111.2, 109.9, 108.9, 67.4, 63.7, 50.5, 26.4; HRMS: m/z (ESI) calc for $C_{18}H_{21}N_2O_2$ ($M+H^+$) 297.15975,

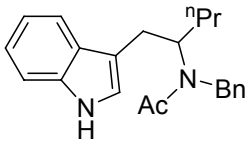
found 297.15973; IR(film): ν [cm^{-1}] = 3410 (s), 2925 (s), 1615 (s), 1515 (s), 1457 (m), 1395 (s), 1245 (s), 1181 (s), 910 (s), 747 (s);



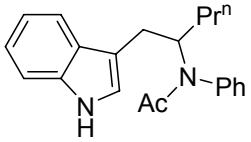
3-(2-Piperidin-1-yl-2-pyridin-3-yl-ethyl)-1H-indole, (Table 7, Entry 10), (15i)
The general procedure B was followed with 3-(1-piperidin-1-yl-allyl)-pyridine (264 mg, 1.30 mmol), phenylhydrazine (141 mg, 1.30 mmol), Rh(acac)$(CO)_2$ (4.7 mg, 0.013 mmol) and XANTPHOS (75 mg, 0.13 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (162 mg, 41 % yield) of the title compound as brown solid. $[\alpha]_D^{20}$ = -42.6 (c = 1.21, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.40-8.35 (m, 2H), 7.88 (bs, 1H), 7.55-7.48 (m, 2H), 7.26 (d, 1H, *J* = 8.1 Hz), 7.15-7.10 (m, 2H), 7.06 (t, 1H, *J* = 7.3 Hz), 6.63 (d, 1H, *J* = 1.5 Hz), 3.77 (dd, 1H, *J* = 4.3 Hz, *J* = 9.5 Hz), 3.47 (dd, 1H, *J* = 3.0 Hz, *J* = 14.0 Hz), 3.14 (dd, 1H, *J* = 10.3 Hz, *J* = 14.0 Hz), 2.48 (bs, 4H), 1.70-1.55 (m, 4H), 1.42-1.36 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 150.2, 148.2, 136.0, 135.9, 134.5, 127.4, 122.9, 122.5, 121.8, 119.1, 118.5, 112.6, 111.0, 68.3, 51.4, 27.9, 26.1, 24.45; HRMS: m/z (ESI) calc for $C_{20}H_{24}N_3$ ($M+H^+$) 306.19647, found 306.19616; IR(film): ν [cm^{-1}] = 3467 (w), 3165 (m), 2922 (vs), 2843 (s), 1720 (s), 1615 (s), 1589 (s), 1464 (vs), 1365 (m), 1249 (s), 1088 (s), 741 (vs).



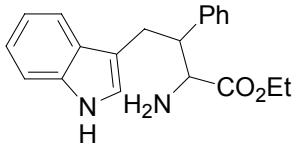
***N*-Benzyl-*N*-[1-(1H-indol-3-ylmethyl)-propyl]-acetamide, (Table 7, Entry 11), (15j)**
The general procedure A was followed with *N*-benzyl-*N*-(1-ethyl-allyl)-acetamide (245 mg, 1.13 mmol), phenylhydrazine (122 mg, 1.13 mmol), Rh(acac)$(CO)_2$ (4.7 mg, 0.011 mmol) and XANTPHOS (65.4 mg, 0.113 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/ethylacetate/triethylamine = 1/1/0.1) to give (214 mg, 59 % yield) of the title compound as brownish oil. $[\alpha]_D^{20}$ = -54.4 (c = 1.02, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.77, 8.69 (2 bs, 1H), 7.53, 7.47 (2 d, 1H, *J* = 7.8 Hz), 7.38-7.04 (m, 8H), 6.99, 6.66 (2 s, 1H), 4.71, 4.55 (2 d, 1H, *J* = 15.4 Hz), 4.33 (dd, 1H, *J* = 17.4 Hz, *J* = 43.0 Hz), 4.02 -3.95, 3.07-3.02 (2 m, 1H), 2.95-2.85 (m, 2H), 2.05,1.81 (2 s, 1H), 1.70-1.59 (m, 2H), 0.92-0.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.2 (s, C), 139.3 (s, C), 137.8, 136.1 (2s, C), 127.5, 126.9 (2s, C), 128.5, 128.2, 127.9, 127.1, 126.7, 126.3, 122.9, 122.4, 121.7, 121.5, 119.2, 118.9, 118.5, 117.8 (14d, 7xCH), 112.6, 111.4 (2s, C), 111.5, 111.1 (2d, CH), 61.8 (d, CH), 43.9 (t, CH_2), 29.4, 28.4 (2t, CH_2), 26.4, 25.2 (2 t, CH_2), 22.9, 22.0 (2q, CH_3), 11.4, 11.3 (2q, CH3); HRMS: m/z (ESI) calc for $C_{21}H_{25}N_2O$ ($M+H^+$) 321.19614, found 321.19619; IR(film): ν [cm^{-1}] =3412 (m) , 3280 (bs), 2955 (s), 2925 (s), 2860 (s), 1580 (s), 1495 (m), 1440 (m), 1333 (m), 1305 (m), 1240 (m), 1160 (w), 1106 (m), 974 (m), 742 (s).



_N_-benzyl-_N_-[1-(1H-indol-3-ylmethyl)-butyl]-acetamide, (Table 7, Entry 12), (15k)
The general procedure A was followed with _N_-benzyl-_N_-(1-propyl-allyl)-acetamide (405 mg, 1.75 mmol), phenylhydrazine (190 mg, 1.75 mmol), $Rh(acac)(CO)_2$ (6.3 mg, 0.017 mmol) and XANTPHOS (101 mg, 0.17 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE/triethylamine = 1/1/0.1) to give (445 mg, 76 % yield) of the title compound as yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 91 % [Diacel Chiralcel OD (0.46 cm x 25 cm, 5 μm); heptane/2-propanol = 95/5; flow rate = 1.5 ml/min; detection wavelength = 254 nm; TR = 17.0 (-), 19.5 (+) min]. $[\alpha]_D^{20}$ = + 26.2 (_c_ = 0.992, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.69, 8.61 (2 bs, 1H, NH), 7.53, 7.46 (2d, 1H, _J_ = 7.8 Hz, CH), 7.40-7.04 (m, 8H, 8 x CH), 7.02, 6.67 (2 d, 1H, _J_ = 1.8 Hz, _J_ = 2.1 Hz, CH), 4.79, 4.47 (2 d, 1H, _J_ = 15.3 Hz, CH_H_), 4.38, 4.32 (2d, 1H, _J_ = 17.4 Hz, C_H_H), 4.10-4.02, 3.08-3.01 (m, 1H, CH), 2.94-2.84 (m, 2H, CH2), 2.04, 1.77 (2 s, 3H, CH3), 1.61-1.51 (m, 2H, CH2), 1.32-1.20 (m, 2H, CH2), 0.81, 0.74 (2 t, 3H, _J_ = 7.3 Hz, CH3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 172.2 (s, C), 139.7 (s, C), 136.3, 128.7, 128.4, 128.2 (s, C), 127.8, 127.3, 126.9, 126.5, 123.0 (s, C), 122.5, 122.2, 121.9, 119.6, 119.3, 118.9 (d, CH), 118.1 (d, CH), 113.0 (s, C), 111.6, 111.2 (2 d, CH), 60.1 (d, CH), 46.0 (t, CH2), 35.9, 34.7 (2 t, CH2), 29.8, 28.9 (2 t, CH2), 23.2, 22.2 (2 q, CH3), 20.3, 20.1, (2 t, CH2), 14.1, 13.9 (2 q, CH3); HRMS: m/z (FAB) calc for $C_{22}H_{27}N_2O$ ($M+H^+$) 335.2123, found 335.2129; IR(film): ν [cm^{-1}] = 3412 (m) , 3296 (bs), 2955 (s), 2925 (s), 2870 (s), 1560 (s), 1495 (m), 1456 (m), 1340 (m), 1299 (m), 1237 (m), 1162 (w), 1106 (m), 974 (m), 879 (w), 742 (s).

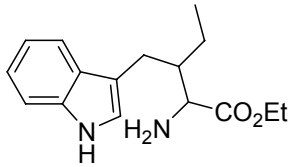


_N_-(1-(1H-indol-3-yl)pentan-2-yl)-_N_-phenylacetamide, (Table 7, Entry 13), (15l)
The general procedure A was followed with _N_-(hex-1-en-3-yl)-_N_-phenylacetamide (100 mg, 0.46 mmol), phenylhydrazine (50 mg, 0.46 mmol), $Rh(acac)(CO)_2$ (1.5 mg, 0.006 mmol) and XANTPHOS (32 mg, 0.055 mmol). The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/MTBE = 1/1) to give (99 mg, 66 % yield) of the title compound as brown oil. $[\alpha]_D^{20}$ = -47.2 (c = 0.46, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$ ppm 8.27 (bs, 1H), 7.52 (d, 1H, _J_ = 7.89 Hz), 7.50-7.28 (m, 5H), 7.23-7.17 (m, 2H), 7.08-7.12 (m, 1H), 5.33 (s, 1H), 2.87 (dd, 1H, _J_ = 15.44 Hz, _J_ = 9.11 Hz), 2.73 (dd, 1H, _J_ = 15.53 Hz, _J_ = 5.91 Hz), 1.74 (s, 3H), 1.59-1.44 (m, 4H), 0.93 (t, 3H, _J_ = 7.05 Hz); ^{13}C NMR (126 MHz, $CDCl_3$ ppm 171.1 (C), 139.5 (C), 136.2 (C), 129.2 (CH), 129.0 (CH), 128.1 (CH), 127.6 (C), 122.2 (CH), 121.8 (CH), 119.2 (CH), 118.7 (CH), 113.2 (C), 111.0 (CH), 60.5 (CH), 35.2 (CH_2), 29.1 (CH_2), 23.7 (CH_3), 20.0 (CH_2), 14.0 (CH_3); HRMS: m/z (ESI) calc for $C_{21}H_{25}N_2O$ ($M+H^+$) 321.1961, found 321.1962; IR(film): ν [cm^{-1}] = 3291 (s), 2957(s), 2928(s), 2870 (m), 1633 (s), 1593 (s), 1494 (s), 1394 (s), 740 (s), 703 (s).



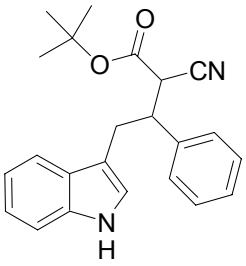
2-amino-4-(1H-indol-3-yl)-3-phenyl-butyric acid ethyl ester (16a)

The general procedure A was followed with ethyl 2-(diphenylmethyleneamino)-3-phenylpent-4-enoate (**12a**+**13a**) (655 mg, 1.7 mmol), phenylhydrazine (186 mg, 1.7 mmol), $Rh(acac)(CO)_2$ (4.4 mg, 0.017 mmol) and XANTPHOS (65 mg, 0.17 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/ethylacetate/triethylamine = 1/2/0.1) to give (334 mg, 61 % yield) of the title compound as yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.22, 8.12 (2s, 1H), 7.65, 7.61 (2d, 1H, *J* = 7.7 Hz), 7.30-7.14 (m, 8H), 6.78, 6.67 (2s, 1H), 4.16-4.06, 4.02-3.92,3.88-3.80 (3m, 2H), 3.73 (d, 1H, *J* = 4.9 Hz), 3.57, 3.50-3.34 (dd, m 2H, *J* = 7.3 Hz, *J* = 12.8 Hz). 3.17 (td, 1H, *J* = 7.7 Hz, *J* = 14.6 Hz), 1.81 (bs, 2H), 1.22, 1.06 (2t, 1H, *J* = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 175.2, 174.5 (2xC), 141.5, 140.2 (2xC), 136.0, 135.9 (2xC), 128.5, 128.4 (2xCH), 128.2, 128.1 (2xCH), 127.5, 127.4 (2xC), 126.9, 126.7 (2xCH), 122.6, 122.4 (2xCH), 121.6, 121.5 (2xCH), 119.0, 118.9 (2xCH), 118.7, 118.6 (2xCH), 113.5, 113.3 (2xC), 111.0, 110.9 (2xCH), 60.8, 60.7($2xCH_2$), 59.2, 57.7 (2xCH), 50.0, 49.3 (2xCH), 27.9, 26.0 ($2xCH_2$), 14.1, 13.8 ($2xCH_3$); HRMS: m/z (ESI) calc for $C_{20}H_{23}N_2O_2$ ($M+H^+$) 323.17540, found 323.17553;



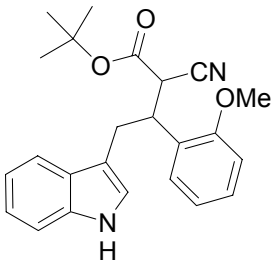
2-amino-3-(1H-indol-3-ylmethyl)-pentanoic acid ethyl ester (16b)

The general procedure A was followed with *N*-benzyl-*N*-(1-propyl-allyl)-acetamide (735 mg, 2.2 mmol), phenylhydrazine (239 mg, 2.2 mmol), $Rh(acac)(CO)_2$ (5.7 mg, 0.022 mmol) and XANTPHOS (85 mg, 0.17 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/ethylacetate/triethylamine = 1/2/0.1) to give (278 mg, 46 % yield) of the title compound as yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.35, 8.29 (2s, 1H), 7.65, 7.58 (2d, 1H, *J* = 7.8 Hz), 7.31 (d, 1H, *J* = 7.8 Hz), 7.12 (dt, 2H, *J* = 7.2 Hz, *J* = 27.7 Hz), 7.00, 6.93 (2s, 1H), 4.05 (dq, 1H, *J* = 7.2 Hz, *J* = 10.9 Hz), 3.86 (dq, 1H, *J* = 7.2 Hz, *J* = 10.9 Hz), 3.60, 3.48 (2d, 1H, *J* = 2.7 Hz), 2.84, 2.73 (2t, 1H, *J* = 8.1 Hz), 2.27-2.19 (m, 1H), 1.59 (bs, 2H), 1.54-1.35 (m, 2H), 1.17 (t, 3H, *J* = 7.1 Hz), 0.97 (t, 3H, *J* = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 175.9, 136.3, 127.6, 122.7, 121.6, 118.9, 118.9, 113.8, 111.0, 60.7, 55.3, 44.0, 25.1, 23.7, 14.0, 11.9; HRMS: m/z (ESI) calc for $C_{20}H_{23}N_2O_2$ ($M+H^+$) 275.17540, found 275.17548; IR(film): ν [cm^{-1}] = 3389 (bs), 3251 (bs), 2948 (s), 2863 (s), 1733 (vs), 1477 (s), 1227 (s), 1188 (s), 1024 (m).



***tert*-butyl 2-cyano-4-(1H-indol-3-yl)-3-phenylbutanoate, (mixture of diastereoisomers), (Table 8, Entry 1), (17a)**

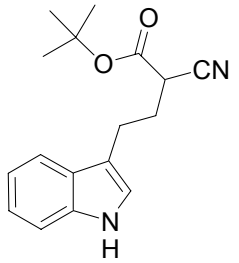
The general procedure was followed with *tert*-butyl 2-cyano-3-phenylpent-4-enoate (53b) (106 mg, 0.41 mmol), phenylhydrazine (55 mg, 0.8 mmol), $Rh(acac)(CO)_2$ (1,07 mg, 0.004 mmol) and XANTPHOS (23 mg, 0.04 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 2/1) to give (88 mg, 60 % yield) of the title compound as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.07 (bs, 1H), 7.90 (bs, 1H), 7.68 (d, 1H, *J* = 7.76 Hz), 7.56 (d, 1H, *J* = 7.82 Hz), 7.47 (d, 2H, *J* = 7.25 Hz), 7.40-7.05 (m, 16H), 3.79-3.67 (m, 4H), 3.51-3.25 (m, 4H), 1.27 (s, 9H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 164.7 (C), 164.5 (C), 128.5 (CH), 128.5 (CH), 128.2 (2xCH), 128.0 (CH), 127.9 (CH), 127.6 (CH), 122.3 (CH), 122.0 (CH), 119.4 (CH), 119.7 (CH), 118.7 (2xCH), 116.6 (C), 116.1 (C), 112.1 (2xC), 111.3 (CH), 111.1 (CH), 83.8 (C), 46.3 (CH), 46.0 (CH), 45.0 (CH), 43.7 (CH), 30.1 (CH_2), 28.8 (CH_2), 27.5 (6xCH_3). IR(film): ν [cm^{-1}] = 3420 (m), 3070 (s), 2922 (s), 2860 (m), 2233 (w), 1737 (vs), 1602 (w), 1508 (m), 1455 (s), 1261 (s), 1017 (m), 741 (vs).



***tert*-butyl 2-cyano-4-(1H-indol-3-yl)-3-(2-methoxyphenyl)butanoate, (mixture of diastereoisomers), (Table 8, Entry 2), (17b)**

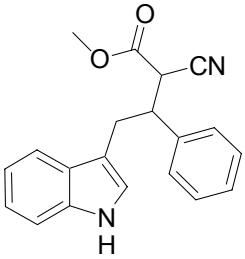
The general procedure was followed with *tert*-butyl 2-cyano-3-(2-methoxyphenyl)pent-4-enoate (200 mg, 0.69 mmol), Phenylhydrazine (75 mg, 0.69 mmol), $Rh(acac)(CO)_2$ (1,96 mg, 0.007 mmol) and XANTPHOS (41 mg, 0.069 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 2/1) to give (101 mg, 37 % yield) of the title compound as brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.11 (s, 1H), 7.95 (s, 1H), 7.74 (d, 1H, *J* = 7.71 Hz), 7.60 (d, 7H, *J* = 7.74 Hz), 7.52 (d, 7H, *J* = 7.52 Hz), 7.37 (d, 1H, *J* = 7.68 Hz), 7.32-7.04 (m, 1H), 6.98-6.76 (m, 1H), 4.30 (td, 1H, *J* = 9.59 Hz, *J* = 6.41 Hz), 4.21-4.11 (m, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.31-3.18 (m, 2H), 3.47-3.33 (m, 2H), 1.24 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 164.8, 164.5 (2xC), 157.1, 157.0 (2xC), 136.3, 136.0 (2xC), 129.2 (CH), 128.5, 128.42 (2xCH), 128.2 (C), 128.0 (CH), 127.5, 127.4 (2xC), 127.2 (C), 123.0, 122.9 (2xCH), 122.0, 121.8 (2xCH), 120.6, 120.4 (2xCH), 119.4, 119.2 (2xCH), 118.8, 118.7 (2xCH), 116.8 (2xC), 112.4, 112.4 (2xC), 111.2, 111.0 (2xCH), 110.6, 110.5

(2xCH), 83.4, 83.4 (2xC), 55.4, 55.3 (2xCH_3), 43.6, 42.3 (2xCH), 40.9 (CH), 38.9 (CH), 29.5 (CH_2), 27.4 (6xCH_3), 26.8(CH_2). IR(film): ν [cm^{-1}] = 3440 (m), 3080 (s), 2922 (s), , 2233 (m), 1733 (vs), 1605 (w), 1510 (m), 1455 (s), 1245 (vs), 1012(m), 741 (vs).



***tert*-butyl 2-cyano-4-(1H-indol-3-yl)butanoate, (Table 8, Entry 3), (17c)**

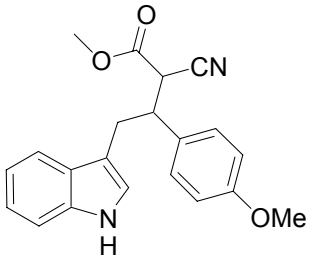
The general procedure was followed with *tert*-butyl 2-cyanohex-5-enoate (300 mg, 1.54 mmol), Phenylhydrazine (166 mg, 1.54 mmol), Rh(acac)$(CO)_2$ (3.52 mg, 0.015 mmol) and XANTPHOS (80 mg, 0.154 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/Ethylacetate = 3/1) to give (251 mg, 57 % yield) of the title compound as yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.22 (s, 1H), 7.63 (d, 1H, *J* = 7.8 Hz), 7.37 (d, 1H, *J* = 8.0 Hz), 7.19 (dt, 2H, *J* = 7.2 Hz, *J* = 14.9 Hz), 7.03 (s, 1H), 3.43 (dd, 1H, *J* = 6.1 Hz, *J* = 8.4 Hz), 3.02 (tq, 1H, *J* = 7.4 Hz, *J* = 14.9 Hz), 2.40-2.34 (m, 1H), 1.50 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 165.1, 136.3, 126.9, 122.2, 122.0, 119.3, 118.4, 116.9, 112.9, 111.2, 83.9, 37.8, 30.1, 27.6, 22.2; HRMS: m/z (FAB) calc for $C_{17}H_{20}N_2O_2$ (M^+) 284.1520, found 284.1515; IR(film): ν [cm^{-1}] = 3415 (s), 2975 (m), 2935 (m), 2252 (w), 1733 (vs), 1457 (s), 1365 (s), 1155 (vs), 748 (s).



methyl 2-cyano-4-(1H-indol-3-yl)-3-phenylbutanoate, (mixture of diastereoisomers) , (Table 8, Entry 4), (17d)

The general procedure was followed with methyl-2-cyano-3-phenylpent-4-enoat (300 mg, 1.4 mmol), Phenylhydrazine (151 mg, 1.4 mmol), Rh(acac)$(CO)_2$ (3.2 mg, 0.014 mmol) and XANTPHOS (73 mg, 0.14 mmol). The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 2/1) to give (174 mg, 39 % yield) of the title compound as yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.18, 8.03 (2 bs, 1 H), 7.68, 7.59 (2d, 1H, *J* = 7.9 Hz, *J* = 8.0 Hz), 7.44 (dd, 1H, *J* = 1.4 Hz, *J* = 6.7 Hz), 7.40-7.13 (m, 6H), 7.03, 6.91 (2 d, 1H, *J* = 7.3 Hz, *J* = 7.6 Hz), 7.12, 6.89 (2d, 1H, *J* = 2.3 Hz, *J* = 1.7 Hz), 4.01 (dd, 1H, *J* = 5.9 Hz, *J* = 12.5 Hz), 3.78-3.72 (m, 1H), 3.91, 3.82, 3.55,3.37 (4 s, 3H), 3.52-3.31 (m, 1H), 2.80-2.38 (m, 1H); 13C NMR (125 MHz, $CDCl_3$) δ ppm 166.3 (s, C), 144.3 (s, C), 139.1, 129.3, 128.9, 128.6, 128.2, 128.1, 128.0, 127.8 (s, C), 127.1,123.8 , 123.3, 122.5 (s, C), 122.2, 121.1, 119.7, 119.3 (2 d, CH), 118.9, 118.8 (2 d, CH), 115.7, 115.6, 113.3 (2 s, C), 112.1, 111.7 (2 s, C), 111.5, 111.3 (2 d, CH), 54.1, 53.2, 53.1, 52.4 (4 q, CH3), 46.0, 44.4 (2 d, CH), 46.1,43.3 (2 d,

CH), 29.7, 28.5, 27.6, 25.9 (4 t, CH2); HRMS: m/z (FAB) calc for $C_{20}H_{19}N_2O_2$ ($M+H^+$) 319.1447, found 319.1490; IR(film): ν [cm^{-1}] = 3415 (m), 3060 (m), 2922 (m), 2863 (m), 2245 (w), 1746 (vs), 1503 (m), 1457 (s), 1267 (m), 1017 (m), 741 (vs).

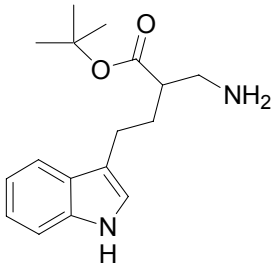


methyl 2-cyano-4-(1H-indol-3-yl)-3-(4-methoxyphenyl)butanoate, (mixture of diastereoisomers), (Table 8, Entry 5), (17e)

The general procedure A was followed with methyl 2-cyano-3-(4-methoxyphenyl)pent-4-enoate (200 mg, 0.8 mmol), phenylhydrazine (86 mg, 0.8 mmol), $Rh(acac)(CO)_2$ (2,16 mg, 0.008 mmol) and XANTPHOS (47 mg, 0.08 mmol).The crude reaction mixture was purified by flash column chromatography on silica gel (cyclohexane/MTBE = 2/1) to give (189 mg, 66 % yield) of the title compound as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.15 (s, 1H), 8.01 (s, 1H), 7.68 (d, 1H, *J* = 7.88 Hz), 7.60 (d, 1H, *J* = 7.84 Hz), 7.41-7.31 (m, 4H), 7.29-7.08 (m, 8H), 6.94-6.83 (m, 6H), 3.81 (s, 3H), 3.81-3.74 (m, 4H), 3.79 (s, 3H), 3.57 (s, 3H), 3.47 (dd, 1H, *J* = 14.70 Hz, *J* = 7.56 Hz), 3.43-3.36 (m, 2H), 3.40 (s, 3H), 3.30 (dd, 1H, *J* = 14.71 Hz, *J* = 5.96 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.2, 165.6 (2xC), 159.3, 159.1 (2xC), 136.4, 136.1 (2xC), 131.9, 130.9 (2xC), 129.9, 128.7 (2xCH), 127.2, 127.0 (2xC), 123.0, 123.5 (2xCH), 122.3, 122.0 (2xCH), 119.7, 119.5 (2xCH), 118.7, 118.6 (2xCH), 116.0, 115.5 (2xC), 114.1, 114.1 (2xCH), 112.1, 111.7 (2xC), 111.3, 111.1 (2xCH), 55.2 ($2xCH_3$), 53.1, 52.9 ($2xCH_3$), 45.2, 45.2 (2xCH), 44.4, 43.3 (2xCH), 29.7, 28.4 ($2xCH_2$); HRMS: m/z (HPLC-ESI) calc for $C_{21}H_{21}N_2O_3$ ($M+H^+$) 349.15467, found 349.15465; IR(film): ν [cm^{-1}] =3446 (m), 2910 (s), 2835 (s) , 2215 (m), 1733 (vs), 1502 (m), 1455 (s), 1255 (vs), 1010(m), 740 (vs).

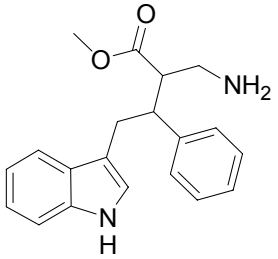
General procedure for reduction of α-cyanoacetate indoles

In a reaction vial containing PTFE septum Cyano indole (40-50 mg, 1 equivalent) and Raney-Co (100-200 mg, qualitative super stoichiometric amount), were dissolved in 3 ml of MeOH and subsequently 4 ml of water was added. Reaction mixture was placed in an autoclave and pressurized with 40 bar of H_2. The reaction is vigorously stirred at 90 °C for 5h. After autoclave is cooled down to room temperature reaction mixture is filtered through sintered glass filter, filer was washed with 50 ml of MeOH and volatiles were removed under reduced pressure to give desired compound without further purification.



2-Aminomethyl-4-(1H-indol-3-yl)-butyric acid *tert*-butyl ester, (18a)

The general procedure was followed with *tert*-butyl 2-cyano-4-(1H-indol-3-yl)butanoate (50 mg, 0.18 mmol) and 150 mg of Raney-Co (3 wt. eq.) The crude reaction mixture was filtered through sintered glass filter to yield title compound (46 mg, 90 % yield) without further purification; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm 8.41 (s, 1H), 7.53 (d, 1H, *J* = 7.6 Hz), 7.30 (d, 1H, *J* = 7.8 Hz), 7.10 (dt, 2H, *J* = 6.9 Hz, *J* = 27.9 Hz), 6.99 (s, 1H), 5.22 (bs, 2H), 2.98 (d, 2H, *J* = 40.3 Hz), 2.80-2.56 (m, 3H), 2.06-1.80 (m, 2H), 1.43 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ ppm 173.9, 136.2, 127.2, 121.9, 121.7, 118.9, 118.6, 114.8, 111.3, 81.5, 46.1, 42.0, 30.1, 28.0, 22.3; HRMS: m/z (ESI) calc for $C_{17}H_{25}N_2O_2$ ($M+H^+$) 289.19105, found 289.19062; IR(film): ν [cm^{-1}] = 3395-2988 (vs), 2055 (w), 1720 (vs), 1641 (s), 1444 (s), 1273 (m), 1142 (s), 741 (vs).



methyl 2-(aminomethyl)-4-(1H-indol-3-yl)-3-phenylbutanoate, (18b)

The general procedure was followed with methyl 2-cyano-4-(1H-indol-3-yl)-3-phenylbutanoate (40 mg, 0.13mmol) and 100 mg of Raney-Co, The crude reaction mixture was filtered through sintered glass filter to yield title compound (42 mg, 100 % yield) without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.93, 8.03 (2 bs,1 H, NH), 7.60-7.47 (m, 1H), 7.40-7.08 (m, 6H), 7.04 (d, 1H, *J* = 7.7 Hz), 6.90 (t, 1H, *J* = 7.3 Hz), 6.71, 6.49 (2d, 1H, *J* = 2.1 Hz, *J* = 1.9 Hz), 4.00, 3.81 (2m, 1 H), 3.90, 3.78, 3.63, 3.46 (4 s, 3 H), 3.38-2.95 (m, 2H), 3.28-3.25, 2.93-2.91 (2 m, 1 H), 2.76-2.32- (m, 2 H); 13C NMR (125 MHz, $CDCl_3$) δ ppm 167.4 (d, C),145.2 (d, C), 135.9, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.1, 127.8 (d, C) ,127.6, 126.7 (d, C) , 122.8, 122.5, 121.9, 121.7 (2 d, CH) , 121.0, 119.3, 118.8 (d, CH) , 113.3(d, CH) , 112.6, 112.4, 111.6, 111.2 (2 s, C) , 54.0, 53.5, 53.1, 52.3 (4 q, CH3) , 48.7 , 47.4 (2t, CH2) , 45.9 (d, CH) , 46.4, 43.1 (2 d, CH) , 30.2, 27.6, 26.9,25.9 (4 t, CH2); HRMS: m/z (FAB) calc for $C_{20}H_{23}N_2O_2$ ($M+H^+$) 323.1760, found 323.1800; IR(film): ν [cm^{-1}] =3440-2955 (vs), 2063 (w), 1731 (vs), 1645 (s), 1440 (s), 1241 (s), 1142 (s), 1010 (vs).