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SUPPORTING INFORMATION

Chiral Lewis Acid Catalysis in Conjugate Additions of *O*-Benzylhydroxylamine to Unsaturated Amides. Enantioselective Synthesis of β-Amino Acid Precursors.

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Experimental Procedures. Methylene chloride, acetonitrile, and triethylamine were distilled from calcium hydride. Tetrahydrofuran, toluene, and benzene were distilled from benzophenone/ketyl prior to use. Methanol was distilled from Mg/I_2. Magnesium bromide-etherate was either purchased from Aldrich chemicals or freshly prepared from magnesium and dibromoethane (Pohmakotr, M.; Geiss, K.-H.; Seebach, D. *Chem. Ber.* **1979**, *112*, 1420). Thin layer chromatographic analyses were performed on silica gel Whatmann-60F glass plates and components were visualized by illumination with UV light or by staining with phosphomolybdic acid. Flash chromatography were performed using E. Merck silica gel 60 (230-400 mesh). Melting points were determined using a Thomas Hoover capillary melting point apparatus or Fisher-Johns melting point apparatus. All glassware was oven/and or flame dried, assembled hot, and cooled under a stream of dry nitrogen or argon before use. Reactions with air sensitive materials were carried out by standard syringe techniques.

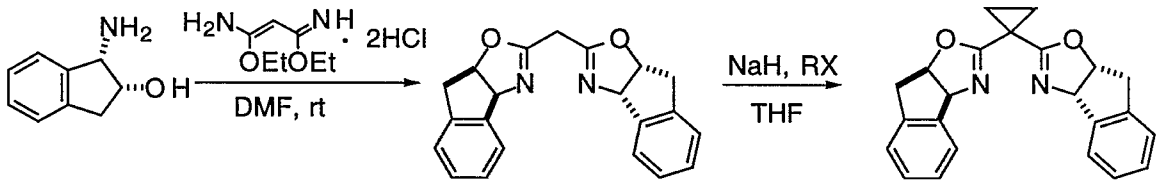
^1H NMR were recorded on a JEOL GSX-400 (400 MHz), JEOL GSX-270 (270 MHz) spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual $CHCl_3$ (7.27 ppm) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublets of doublets, m = multiplet, br = broad), integration and coupling constant(s). ^{13}C NMR were recorded on a JEOL-GSX-400 (100 MHz) and JEOL GSX-270 (65 MHz) spectrometers using broad band proton decoupling. Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard. HPLC analyses were carried out on either an ISCO system comprising of a 2360 pump, 2350 gradient programmer and a V^4 variable wavelength UV detector connected to a Hewlett-Packard 3396 II integrator or a Waters M-45 pump connected to an ISCO 228 Absorbance Detector with a type 6 optical unit and a Hewlett-Packard 3396-II integrator. Rotations were recorded on a JASCO-DIP-370 instrument.

Elemental analyses were performed in house on a Perkin Elmer Series II CHNS/O Analyzer 2400.

Starting α,β-unsaturated pyrazole amide 1. The synthesis of pyrazole crotonate (**1**) has been described in the literature (Kashima, C.; Harada, H.; Kita, I.; Fukuchi, I.; Hosomi, A. *Synthesis* **1994**, 61).

Preparation of Bisoxazoline Ligand 2: Under N_2, 2.5 equivalents of amino indanol was added to a rapidly stirred suspension of ethyl 3-amino-3-ethoxyprop-2-enimidate (Hall, J.; Lehn, J-M.; DeCian, A.; Fischer, J. *Helv. Chim. Acta* **1991**, *74*, 1) in dry DMF (1g/10 mL) at 0 °C. The white suspension was almost completely solubilized before new solid began to precipitate. The ice-bath was removed and the mixture was stirred at rt for 3 days. Most of DMF was removed under vacuum at rt. The residue was then diluted with CH_2Cl_2, washed with brine and dried over $MgSO_4$. The product was purified by recrystallization from ethanol, and used in the next step.

Preparation of Spirobisoxazoline Ligand: Under N_2, to a solution of dihydrobisoxazoline (0.2 M) in THF, was added 3 equivalents of NaH (60%) in portions at 0 °C. After complete addition, the mixture was stirred for 30 minutes at 0 °C. A solution of $Br(CH_2)_2Br$ (1.2 equivalents) in THF was then added dropwise at 0 °C over 10 minutes and the mixture was then heated to 50 °C and the reaction was completed within 0.5-2h. The reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The extracts were combined, washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified by chromatography on silica gel (2% MeOH/EtOAc) followed by recrystallization using EtOAc/hexane.



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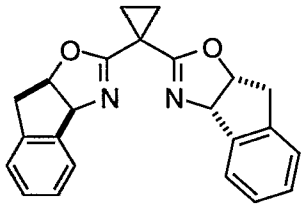


{3a*S*-[2(3'a*R, 8'a*S**), 3aα, 8aα]}-2,2'-(cyclopropylidene)-bis{3a, 8a-dihydro-8H-indeno[1,2-*d*]-oxazole} (2):** mp. 163-164 °C (EtOAc/hexane); R_f 0.20 (90:10-ethyl acetate:MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 1H), 7.25-7.19 (m, 3H), 5.50 (d, J=8.0 Hz, 1H), 5.33-5.24 (m, 1H), 3.36 (dd, J=18.0, 7.0 Hz, 1H), 3.17 (d, J=17.5 Hz, 1H), 1.37-1.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 141.9, 139.8, 128.4, 127.4, 125.7, 125.2, 83.4, 76.5, 39.7, 18.4, 15.9; $[\alpha]_D^{20}$ -349.28° (c=1.185, CH_2Cl_2).

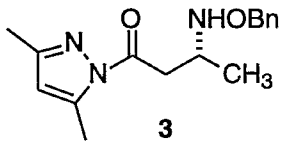
Preparation of H_2NOBn: *O*-Benzylhydroxylamine hydrochloride was washed with 1 M NaOH then extracted with CH_2Cl_2. The combined organics were dried ($MgSO_4$) and concentrated to afford the desired oil.

Representative experimental procedure for stoichiometric Lewis acid-mediated addition. (Table 1, entry 5): Under N_2, to a flask containing $MgBr_2.Et_2O$ (0.1 mmol) and bisoxazoline **2** (0.1 mmol) was added CH_2Cl_2 (3 mL). Pyrazole crotonate **1** (0.1 mmol) (in 1 mL CH_2Cl_2) was added and the mixture was allowed to stir for 30 min. The reaction was cooled to -60 °C then H_2NOBn (0.11 mmol) (in 1.1 mL CH_2Cl_2) was added. The reaction was monitored by TLC and when judged complete was quenched with H_2O and extracted 3 x CH_2Cl_2. The combined organics were dried ($MgSO_4$) and concentrated to give an oil. The product was purified by preparative TLC or silica gel chromatography. The enantiomeric purity was determined by HPLC.

Substoichiometric Chiral Lewis Acid-mediated addition (Table 3, entry 2): Under N_2, to a flask containing $MgBr_2.Et_2O$ (0.15 mmol) and bisoxazoline **2** (0.15 mmol) was added 20 mL CH_2Cl_2. Pyrazole pentenoate **6a** (0.5 mmol) (in 5 mL CH_2Cl_2) was added and stirred for 30 min. The reaction was cooled to -60 °C the H_2NOBn (0.55 mmol) (in 5.5 mL CH_2Cl_2) was added. The reaction was monitored by TLC and when judged complete was quenched with H_2O and extracted 3 x CH_2Cl_2. The combined organics were dried ($MgSO_4$) and concentrated to give an oil. The product was purified by preparative TLC or silica gel chromatography. The enantiomeric purity was determined by HPLC. **Note:** If the reactions are incomplete, it is important to fully quench the Lewis acid and care should be taken to remove solvents at low temperature during workup. This will ensure that addition at higher temperature does not occur leading to lowered selectivity.

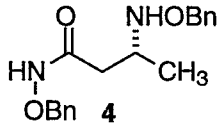
Stoichiometric kinetic resolution (Table 2, entry 1) : Under N_2, to a flask containing $MgBr_2.Et_2O$ (0.1 mmol) and bisoxazoline **2** (0.1 mmol) was added CH_2Cl_2 (4 mL). Racemic **3** (0.1 mmol) (in 0.9 mL CH_2Cl_2) was added and the mixture was allowed to stir for 30 min. The reaction was cooled to -60 °C then the appropriate amount of 0.1 M

H_2NOBn in CH_2Cl_2 was added. After 3 h the reaction was quenched with H_2O and extracted with CH_2Cl_2. The combined organics were dried ($MgSO_4$) and concentrated. The products were purified by preparative TLC (50% EtOAc/hexanes).



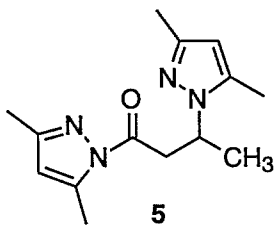
3

Compound 3: ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 5H), 5.93 (s, 1H), 5.84 (bs, 1H), 4.68 (s, 2H), 3.67 (m, 1H), 3.40 (dd, 1H, J=16.9 and 7.5 Hz), 3.32 (dd, 1H, J=16.9 and 5.1 Hz), 2.49 (s, 3H), 2.22 (s, 3H), 1.21 (d, 1H, J=6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 151.9, 144.1, 137.9, 128.4, 128.3, 127.8, 111.2, 76.7, 53.0, 39.5, 18.4, 14.7, 13.9; TLC Rf 0.32 (30% EtOAc/70% hexanes); HPLC [(Column: Chiralcel OJ (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.)]: 254 nm; solvent: hexane:i-PrOH=90:10, flow rate= 1 mL/min. Rt 8 min (R-isomer); Rt 12 min (S-isomer)]; Analysis Calc'd for $C_{26}H_{21}N_3O_2$: C, 66.88; H, 7.37; N, 14.62; found: C, 67.10; H, 7.13; N, 14.51.



4

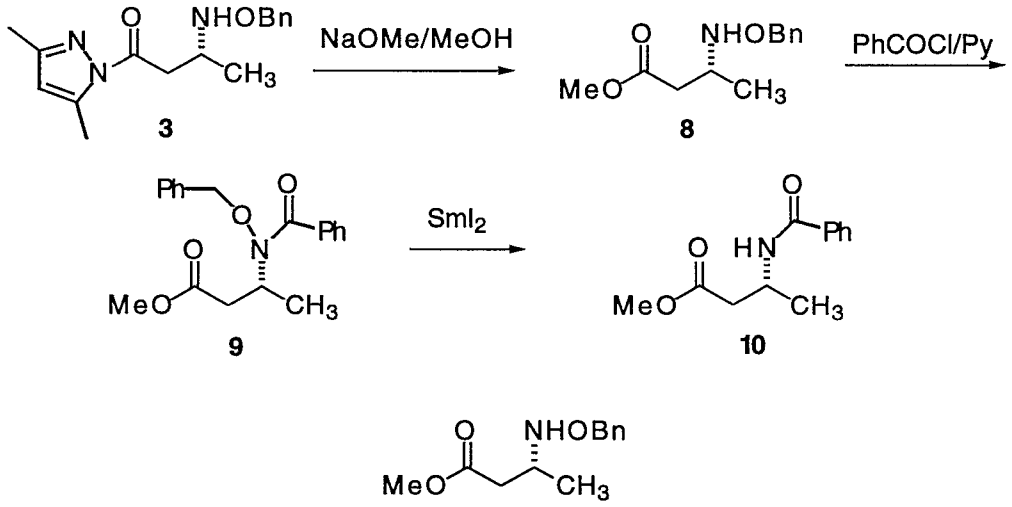
Amidolysis Product 4: ^1H NMR (400 MHz, $CDCl_3$) δ 9.27 (bs, 1H), 7.37-7.23 (m, 10H), 5.41 (bs, 1H), 4.86 (m, 2H), 4.50 (dd, 2H, *J*= 11.5, 15.3 Hz), 3.32, (m, 1H), 2.32-2.20 (m, 2H), 1.07 (d, 3H, J=6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 137.4, 135.7, 129.2, 128.8, 128.7, 128.6, 128.5, 128.1, 78.0, 76.4, 52.9, 37.8, 17.9; TLC Rf 0.14 (50% EtOAc/50% hexanes)HPLC [(Column: Chiralcel AD (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) [254 nm; solvent: hexane:i-PrOH=95:5, flow rate= 1 mL/min. Rt 31 min S isomer; Rt 35 min R-isomer] Analysis Calc'd for $C_{18}H_{22}N_2O_3$: C, 68.77; H, 7.05; N, 8.91; found: C, 68.54; H, 6.98; N, 8.68.



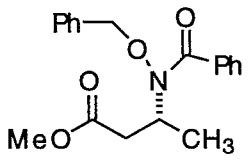
5

Pyrazole Addition Product 5: mp 91-93 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (s, 1H), 5.67 (s, 1H), 4.79 (m, 1H), 3.86 (dd, 1H, J=7.8 and 17.2 Hz), 3.41 (dd, 1H, J= 5.6 and 17.2 Hz), 2.41 (s, 3H), 2.24 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H), 1.48 (d, 3H, J=6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 152.0, 147.3, 143.8, 138.4, 111.1, 104.5, 49.1, 42.3, 21.3, 14.4, 13.82, 13.78, 11.0; TLC Rf 0.25 (30% EtOAc/70% hexanes); Analysis Calc'd for $C_{14}H_{20}N_4O$: C, 64.59, H, 7.74; N, 21.52; found: C, 64.79; H, 7.63; N, 21.67.

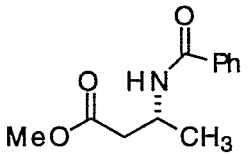
Determination of absolute stereochemistry of (3) by conversion to a known compound. A modified procedure of Falborg and Jorgensen (Falborg, L.; Jorgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2823) was used



Methyl 3-benzyloxyaminobutanoate (8): To a solution of **3** (0.35 mmol) (84% ee) dissolved in 3.5 mL MeOH was added catalytic NaOMe (~10 mg) and stirred at rt for 1 h. The reaction was quenched with solid NH_4Cl and subsequently filtered. The product was purified by SiO_2 chromatography to yield 70.9 mg (90%) of the desired product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (bs, 1H), 7.34-7.22 (m, 5H), 4.68 (s, 2H), 3.64 (s, 3H), 3.47 (m, 1H), 2.59 (dd, 1 H, J=23.1 and 10.5 Hz), 2.35 (dd, 1H, J=23.1 and 8.6 Hz), 1.11 (d, 3H, J=9.6 Hz).

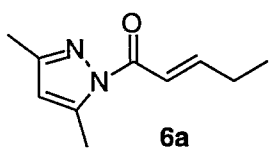


Methyl 3-(*N*-benzoyl-N-benzyloxyamino)butanoate (9): To a solution of methyl ester **8** (84%ee) (0.3176 mmol) in 3 mL THF and pyridine (0.62 mmol) was added benzoyl chloride (0.52 mmol) dropwise and stirred for 30 min. Then another portion of pyridine (0.62 mmol) and benzoyl chloride (0.52 mmol) were added and the reaction stirred for 45 min. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The combined organics were washed with brine, dried ($MgSO_4$) and concentrated. The product was purified by SiO_2 chromatography to yield 90.2 mg (91%) of the desired product: ^1H NMR (270 MHz, $CDCl_3$) δ 7.64-7.60 (m, 2H), 7.49-7.17 (m, 8H), 4.79-4.67 (m, 3H), 3.64 (s, 3H), 2.85 (dd, 1H, J=15.7 and 8.3 Hz), 2.49 (dd, 1H, J=15.7 and 6.0 Hz) 1.31 (d, 3H, J=6.7 Hz).



Methyl 3-benzoylaminobutanoate (10): To a solution of methylester **9** (84%ee) (0.236 mmol) in 2 mL THF was added a 0.1 M THF solution of SmI_2 (9.6 mL, 0.96 mmol) [prepared by mixing samarium (1.2 mmol) and I_2 (1.0 mmol) in 10 mL of THF in an ultrasonic bath for 3 h] until a blue color persisted. After 5 min, the reaction was diluted with CH_2Cl_2 and to it was added 5% sodium thiosulfate solution. The reaction mixture was extracted with CH_2Cl_2 and the combined organics washed with 1M HCl, brine, and dried ($MgSO_4$). The product was purified by SiO_2 chromatography to yield 20.8 mg (40%) of the desired product: ^1H NMR (270 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.50-7.33 (m, 3H), 6.97 (bs, 1H), 4.55 (m, 1H), 3.70 (s, 3H), 2.67 (dd, 1H, J=16.0 and 5.3 Hz), 2.59 (dd, 1H, J=16.0 and 4.7 Hz), 1.31 (d, 3H, J=6.9); $[\alpha]^{25}_D$=35.7° (c 1.04, $CHCl_3$) {lit $[\alpha]^{25}_D$=-40.8° (c 1.0, $CHCl_3$) (*S*) enantiomer (Amoroso, R.; Cardillo, G.; Sabatino, P.; Tomasini, C.; Trere, A. *J. Org. Chem.* **1993**, *58*, 5615)}; [lit $[\alpha]^{25}_D$=-42° (c .77, $CHCl_3$) (*S*) enantiomer (Estermann, H.; Seebach, D. *Helv Chim Acta* **1988**, *71*, 1824)]. The sign of the rotation for the final compound indicates that it has the *R* configuration. The ee calculates to 85% for **10** consistent with the 84% ee for **3**.

Preparation of starting materials for Table 3: Substrate 6a:

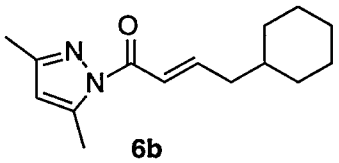


6a

Preparation of E-2-pentenoyl chloride: Under N_2, to a 100 mL flask containing 4 mL (40 mmol) trans-2-pentenoic acid, was added 7 mL (80 mmol) oxalyl chloride. Reaction was initiated by one drop of DMF. The reaction mixture was kept stirring for 20 min at 0 °C, then slowly warmed up to room temperature. The excess oxalyl chloride was removed under vacuum and the product was used without further purification.

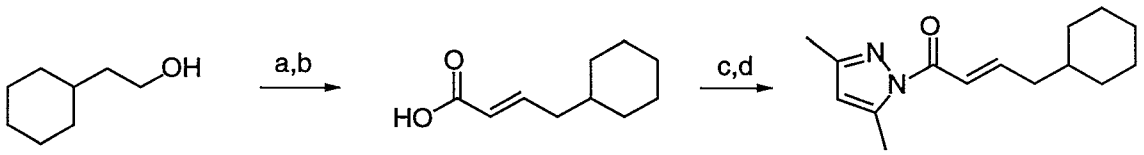
Preparation of 6a: Under N_2, to a 250 mL flask containing 1.7 g (18.2 mmol) of 3,5-dimethyl pyrazole in 1.8 mL (22 mmol) pyridine and 40 mL CH_2Cl_2 at 0 °C was added E-2-pentenoyl chloride (20 mmol in 5 mL CH_2Cl_2) and stirred for 3 hours. The reaction was quenched with 40 mL H_2O and extracted with 3 x CH_2Cl_2. The combined organic extracts were washed with brine, dried with $MgSO_4$ and concentrated to afford an oil. The product was purified by silica gel chromatography (10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25- 7.16 (m, 2H), 5.91 (s, 1H), 2.51 (s, 3H), 2.33-2.26 (m, 2H), 2.20 (s, 3H), 1.08 (t, 3H, J=7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 153.0, 151.8, 144.4, 120.3, 111.3, 26.0, 14.7, 13.9, 12.4; TLC Rf 0.50 in 10% EtOAc/hexanes; Analysis Calc'd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72; found: C, 67.20; H, 7.57; N, 15.62.

Substrate 6b



6b

The desired starting material was prepared using the following reaction sequence.



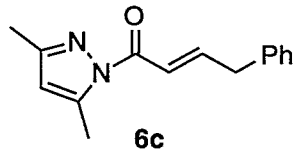
6d

Key: (a) PCC/CH_2Cl_2, 60%, (Upadhya, T. T.; Sudalai, A. *Tetrahedron: Asymmetry* **1997**, *8*, 3685) (b) Diethylphospanoacetic acid, 2.1 eqs n-BuLi, -78 °C, 68%; (c) oxalyl chloride, quantitative; (d) 3,5-dimethylpyrazole, pyridine, CH_2Cl_2, 0 °C, 93%.

6b: The compound was purified by silica gel column chromatography using CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.15 (m, 2H), 5.96 (s, 1H), 2.56 (2, 3H), 2.24 (s, 3H), 2.21 (appt t, 2H, J=6.7 Hz), 1.73-1.61 (m, 5H), 1.51-1.43 (m, 1H), 1.27-1.10 (m, 3H), 1.00-0.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 151.9, 150.9, 144.5, 121.9, 111.3, 40.7, 37.6, 33.3, 26.4, 26.3, 14.8, 13.9; TLC Rf 0.58 in 20% EtOAc/hexanes;

Analysis Calc'd for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37; found: C, 73.45; H, 9.07; N, 11.46.

Substrate 6c:

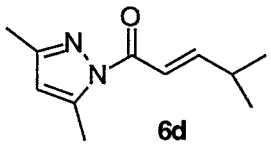


6c

Compound **6c** was prepared according to the methodology described for **6b** using commercially available phenylacetaldehyde. The compound was purified by silica gel column chromatography using 15% ether/hexane. The product was recrystallized from hexane.

6c: mp 34-36 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.21 (m, 7H), 5.98 (s, 1H), 3,66 (d, 2H, J=7.0 Hz), 2.57 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 152.0, 149.1, 144.5, 137.9, 128.83, 128.78, 126.7, 122.2, 111.5, 39.1, 14.8, 13.9; TLC Rf 0.56 in 20% EtOAc/hexanes; Analysis Calc'd for $C_{15}H_{16}N_2O$: C, 74.97, H, 6.71; N, 11.66; found: C, 74.58; H, 6.78; N, 11.73.

Substrate **6d**



6d

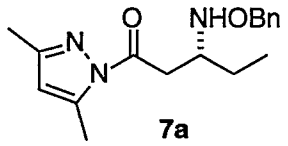
Preparation of (E)-4-Methyl-2-pentenoic acid: Under N_2, to a 500 mL flask containing 200 mL THF and 25.2 mL of 2.5 M BuLi (62 mmol), was added dropwise 5.88 g (30 mmol) of diethylphosphonoacetic acid in 30 mL THF. The solution was stirred at -78 °C for 30 min then 3.3 mL(36 mmol) of isobutyraldehyde in 20 mL THF was added. The reaction mixture was stirred for another 15 min, then warmed up to room temperature. The resulting mixture was diluted with 150 mL 50% ether/50 %hexanes and acidified with 300 mL 1 M HCl solution. The organic layer was washed 2x 100 mL 0.01 M HCl solution and then concentrated to afford an oil. This oil was diluted in 50 mL CH_2Cl_2 and washed with excess 1 M NaOH solution. The aqueous layer was acidified with 1 M HCl solution and then extracted with 2x CH_2Cl_2 .The combined organic extracts were dried

with $MgSO_4$ and concentrated to afford an oil. The carboxylic acid was converted to **6d** following the reaction sequence described for **6b.**

Substrate 6d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.07 (m, 2H), 5.83 (s, 1H), 2.49-2.44 (m, 4H), 2.11 (s, 3H), 1.01 (d, 3H, J=0.81 Hz), 0.99 (d, 3H, J=0.81 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 157.4, 151.5, 144.2, 118.5, 111.1, 31.6, 21.3, 14.6, 13.7; TLC Rf 0.47 in CH_2Cl_2; Analysis Calc'd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57; found: C, 68.69; H, 8.26; N, 14.34. The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent.

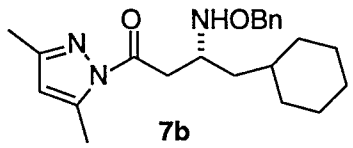
The cinnamate (**6e**) has been reported in the literature (Besida, J.; Brown, R. F. C.; Colamanet, S.; Leach, D. N. *Aust. J. Chem.* **1982**, *35*, 1373)

Conjugate Addition Products for Table 3:



7a

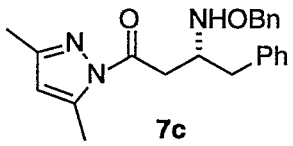
Compound 7a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 5H), 5.94 (s, 1H), 5.93 (s, 1H), 4.65 (s, 2H), 3.42-3.36 (m, 2H), 3.15 (m, 1H), 2.49 (s, 3H), 2.22 (s, 3H), 1.67 (m, 1H), 1.54 (m, 1H), 0.98 (t, 3H, J=7.5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 151.9, 144.1, 138.0, 128.4, 128.3, 127.7, 111.2, 76.5, 58.9, 37.5, 25.2, 14.7, 13.9, 10.7. TLC Rf 0.62 (30% EtOAc/70% hexanes); HPLC [(Column: Chiralcel OJ (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.)]: 254 nm; solvent: hexane:i-PrOH=98:2, flow rate= 1 mL/min. Rt 8 min (major) ; Rt 11 min (minor)]. Analysis Calc'd for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69; N, 13.94; found: C, 67.99; H, 7.63; N, 14.05.



7b

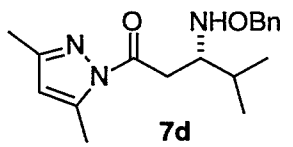
Compound 7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 5H), 5.93 (s, 1H), 5.87 (s, 1H), 4.64 (s, 2H), 3.61 (m, 1H), 3.42 (dd, 1H, J=8.1 and 16.6 Hz), 3.12 (dd, 1H, J=4.3 and 16.6 Hz), 2.49 (s, 3H), 2.22 (s, 3H), 1.74-1.63 (m, 5H), 1.53-1.12 (m, 6H), 0.94-0.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 151.8, 144.0, 138.0, 128.4, 128.3, 127.7,

111.1, 76.5, 54.9, 40.1, 38.4, 34.5, 33.6, 33.5, 26.7, 26.39, 26.36, 14.7, 13.9; TLC Rf 0.44 (30% EtOAc/70% hexanes); HPLC [(Column: Chiralcel OD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.)] [254 nm; solvent: hexane:i-PrOH=99:1, flow rate= 0.25 mL/min. Rt 33 min (major); Rt 45 min (major)]; Analysis Calc'd for $C_{22}H_{31}N_3O_2$: C, 71.51, H, 8.46; N, 11.37; found: C, 71.41; H, 8.51; N, 11.50.



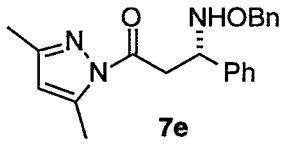
7c

Compound 7c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 10H), 5.95 (s, 1H), 5.89 (s, 1H), 4.70 (s, 2H), 3.82 (m, 1H), 3.51 (dd, 1H, J=7.8 and 16.6 Hz), 3.19 (dd, 1H, J=4.8 and 16.6 Hz), 3.04 (dd, 1H, J=7.5 and 13.7 Hz), 2.85 (dd, 1H, J=6.7 and 13.7 Hz), 2.51 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 151.9, 144.1, 138.5, 137.9, 129.6, 128.6, 128.5, 128.4, 127.8, 126.6, 111.2, 76.6, 59.0, 38.4, 37.5, 14.7, 14.0; TLC Rf 0.54 (30% EtOAc/70% hexanes); HPLC [(Column: Chiralcel OD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.)] 254 nm; solvent: hexane:i-PrOH=98:2, flow rate= 1 mL/min. Rt 9 min (major); Rt 13 min (minor)] Analysis Calc'd for $C_{22}H_{25}N_3O_2$: C, 72.70, H, 6.93; N, 11.56; found: C, 72.34; H, 6.90; N, 11.43.



7d

Compound 7d: mp 30-32 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 5H), 5.93 (s, 2H), 4.62 (s, 2H), 3.39-3.26 (m, 2H), 3.13 (dd, 1H, J=15.8 and 3.0 Hz), 2.48 (s, 3H), 2.22 (s, 3H), 2.01 (m, 1H), 1.01-0.96 (overlapping doublets, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 151.8, 144.1, 138.0, 128.4, 128.3, 127.7, 111.2, 76.2, 62.7, 34.8, 29.3, 19.4, 18.5, 14.7, 13.9. TLC Rf 0.69 (30% EtOAc/70% hexanes); HPLC [(Column: Chiralcel OJ (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.)] [254 nm; solvent: hexane:i-PrOH=96:4, flow rate= 0.15 mL/min. Rt 40 min (major) ; Rt 45 min (minor)] Analysis Calc'd for $C_{18}H_{25}N_3O_2$: C, 68.54; H, 7.99; N, 13.32; found: C, 68.87; H, 7.78; N, 13.41.



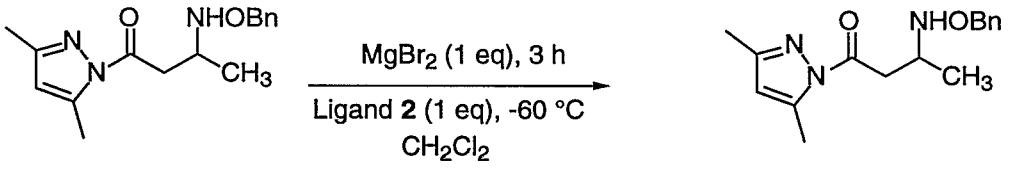
7e

Compound 7e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.19 (m, 10H), 6.08 (s, 1H), 5.92 (s, 1H), 4.69 (dd, 1H, J=5.1 and 8.3 Hz), 4.56 (dd, 2H, J=11.4, 16.0), 3.67 (dd, 1H, J=8.3 and 16.9 Hz), 3.47 (dd, 1H, J=5.1 and 16.9 Hz), 2.46 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 152.1, 144.1, 140.6, 137.7, 128.5, 128.3, 127.9, 127.84, 127.76, 111.3, 111.2, 76.7, 61.5, 39.7, 14.6, 13.9; TLC Rf 0.57 (30% EtOAc/70% hexanes); HPLC [(Column: Chiralcel OJ (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.)] [254 nm; solvent: hexane:i-PrOH=90:10, flow rate= 1 mL/min. Rt 18 min (major); Rt 27 min (minor)]. Analysis Calc'd for $C_{21}H_{23}N_3O_2$: C, 72.18; H, 6.63; N, 12.03; found: C, 72.12; H, 6.71; N, 12.15.

Control Experiments:

Experiment 1:

Following the general procedure outlined for stoichiometric Lewis acid, subjecting racemic **3** to the reaction conditions gave 98% recovered **3** with <1% ee.

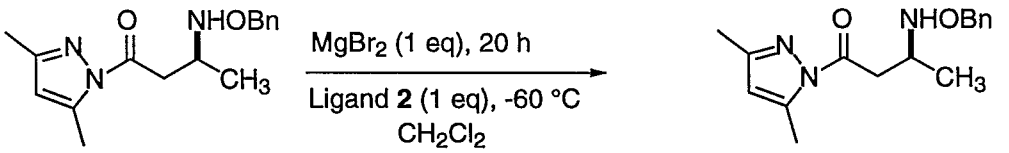


Racemic

98% Recovery
less than 1% ee

Experiment 2:

Following the general procedure outlined for stoichiometric Lewis acid, subjecting **3** (*S*-isomer, 50 %ee) to the reaction conditions gave 90% recovery of **3** with 48% ee with the (*S*)-configuration.

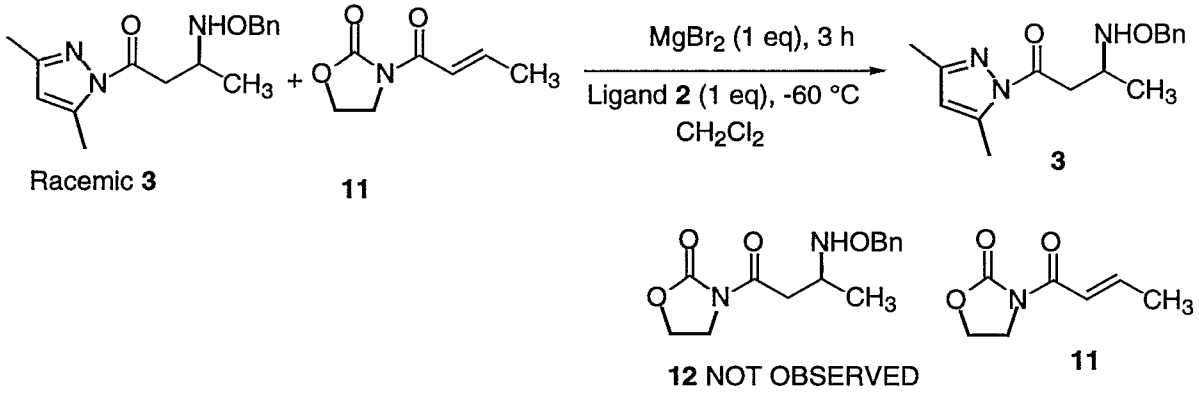


(*S*)-Isomer
50% ee

90% recovery
(S)-isomer 48%ee

Experiment 3: Crossover Experiment

An experiment using racemic **3** and oxazolidinone **11** in the presence of the chiral Lewis acid showed no crossover product **12.**



A control for the crossover experiment using **11** and the standard reaction conditions gave **12.**