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Supporting Information

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Enantioselective Synthesis of Protected Amines via the Catalytic Asymmetric Addition of Hydrazoic Acid to Ketenes

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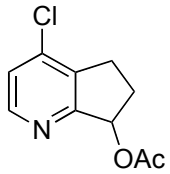
I. General

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

Hexanes, THF, toluene, dichloromethane, and diethyl ether were purified by passage through activated alumina. Concentrated sulfuric acid (99.9%; Aldrich), NaN_3 (Mallinckrodt), acetic anhydride (Alfa Aesar), $FeCl_2$ (anhydrous, 98%; Strem), pentamethylcyclopentadiene (Cp*H; Strem), methylboronic acid (97%; Alfa Aesar), and $Pd(PPh_3)_4$ (99.9%; Strem) were used without further purification. Potassium hydride (30-35% w/w in mineral oil; Alfa Aesar) was washed three times with hexanes, filtered, dried under vacuum, and stored in a glove box. Hydrazoic acid was prepared according to a published procedure.[1,2] All other chemicals were purchased from commercial suppliers and used as received, unless otherwise noted.

II. Synthesis of Catalyst 2

This synthesis has not been optimized.



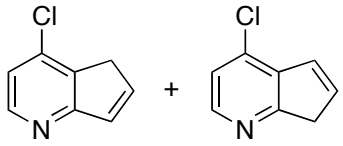
4-Chloro-6,7-dihydro-5*H*-[1]pyrindin-7-yl-ester. Acetic anhydride (8.20 mL, 86.4 mmol, 15.7 equiv) was added to 4-chloro-6,7-dihydro-5*H*-[1]pyrindine-1-oxide[3] (0.85 g, 5.0 mmol) in a 25-mL round-bottomed flask equipped with a reflux condenser. The resulting brown mixture was stirred at room temperature for 20 min and then at 100 °C for 3 h. Next, the brown mixture was allowed to cool to room temperature, and the excess acetic anhydride was removed in vacuo. The dark-brown residue was dissolved in CH_2Cl_2 and purified by flash chromatography (40% EtOAc/hexanes) on silica gel, which afforded the title compound as a pale-yellow oil: 0.70 g (65% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (d, *J* = 5.3 Hz, 1H), 7.22 (d, *J* = 5.3 Hz, 1H), 6.16 (dd, *J* = 7.6, 5.0 Hz, 1H), 3.14-2.97 (m, 1H), 2.97-2.83 (m, 1H), 2.72-2.59 (m, 1H) 2.12 (s, 3H), 2.12-2.04 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 162.1, 149.9, 141.6, 136.4, 123.5, 77.3, 29.9, 27.0, 21.1;

IR (neat) 3057, 2983, 2947, 1740, 1563 cm^{-1};

LRMS (ES/APCI) calcd for $C_{10}H_{10}ClNO_2$ (M+Na$^+$) 234.0, found 234.0.



4-Chloro-5*H*-[1]pyrindine and 4-chloro-7*H*-[1]pyrindine. Concentrated sulfuric acid (1.2 mL) was added via syringe to 4-chloro-6,7-dihydro-5*H*-[1]pyrindin-7-yl-ester (0.59 g, 3.0 mmol) in a 25-mL round-bottomed flask at 0 °C. The mixture was heated to 60 °C and stirred for 1.5 h. The mixture was then allowed to cool to room temperature and poured into ice water (100 mL). The mixture was made basic by slowly adding a 6 M solution of KOH. The aqueous layer was extracted with EtOAc (3 x 5 mL). Et_3N (1 mL) was added to the combined organic layers, which were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography (hexanes/EtOAc/Et_3N = 45/45/10) on silica gel, which afforded the title compound as a 3:1 mixture of 5*H*:7*H* isomers (0.37 g, 91% yield; orange oil).

5*H* Isomer:

^{1}H NMR (C_6D_6, 400 MHz): δ 8.25 (d, *J* = 5.4 Hz, 1H), 6.89 (dt, *J* = 5.6, 1.8 Hz, 1H), 6.63 (d, *J* = 5.4 Hz, 1H), 6.22 (dt, *J* = 5.6, 2.0 Hz, 1H), 2.80-2.79 (m, 2H);

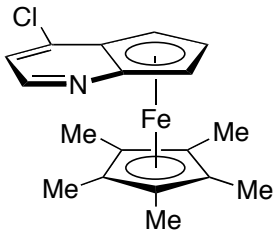
^{13}C NMR (C_6D_6, 100 MHz): δ 166.1, 149.5, 139.3, 135.4, 134.9, 122.8, 119.6, 36.3;

7*H* Isomer:

^{1}H NMR (C_6D_6, 400 MHz): δ 8.06 (d, *J* = 5.5 Hz, 1H), 6.72 (dt, *J* = 6.0, 1.8 Hz, 1H), 6.70 (d, *J* = 5.5 Hz, 1H), 6.02 (d, *J* = 6.0 Hz, 1H), 3.11-3.10 (m, 2H);

^{13}C NMR (C_6D_6, 100 MHz): δ 167.0, 146.6, 138.6, 136.2, 135.1, 133.8, 121.5, 41.5;

IR (neat) 3053, 2907, 2847, 1582, 1559, 1458, 1389, 819 cm^{-1};



4-Chloropyrindinyl-pentamethylcyclopentadienyliron. A solution of *n*-BuLi (3.41 M in hexanes; 0.12 mL, 0.41 mmol, 1.1 equiv) was added dropwise to a solution of Cp*H (55.4 mg, 0.41 mmol, 1.1 equiv) in anhydrous THF (2.0 mL) in a 0 °C ice bath. The

mixture was allowed to warm to room temperature and then stirred for an additional 30 min.

Separately, anhydrous THF (0.8 mL) was added to $FeCl_2$ (57.4 mg, 0.45 mmol, 1.2 equiv), and the resulting mixture was sonicated for 30 min, resulting in a white suspension. Next, the mixture was cooled to 0 °C, and the solution that contained the Cp*Li was added by cannula to the suspension of $FeCl_2$, leading to a green mixture, which was stirred at 0 °C for 30 min.

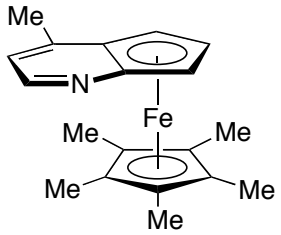
A solution of 4-chloro-5*H*-[1]pyrindine and 4-chloro-7*H*-[1]pyrindine (50.0 mg, 0.37 mmol, 1 equiv) in THF (1.8 mL) was added to a 0 °C mixture of KH (14.8 mg, 0.37 mmol, 1 equiv) and THF (1.8 mL), yielding a red mixture. This mixture was stirred until the evolution of H_2 had ceased (~10 min). This deep red solution was added via cannula to the suspension of Cp*FeCl in THF at 0 °C, leading to the immediate formation of a purple mixture. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. Next, the purple suspension was poured onto a plug of silica gel and eluted with hexanes/EtOAc/Et_3N (1/1/0.1). Removal of the solvent furnished a purple solid, which was purified by flash chromatography (hexanes/EtOAc/Et_3N 4/1/0.1 to 1/1/0.1) on silica gel, which afforded the title compound as a purple solid: 82.5 mg (65% yield).

^{1}H NMR (C_6D_6, 400 MHz): δ 8.27 (d, *J* = 4.2 Hz, 1H), 6.51 (d, *J* = 4.2 Hz, 1H), 4.80 (d, *J* = 1.6 Hz, 1H), 4.38 (d, *J* = 1.7 Hz, 1H), 3.66 (t, *J* = 2.6 Hz, 1H), 1.55 (s, 15H);

^{13}CNMR (C_6D_6, 100 MHz): δ 150.3, 147.1, 115.5, 111.0, 82.0, 78.6, 77.3, 68.4, 62.5, 9.7;

IR (neat) 3440, 2902, 1584, 1491, 1298, 1032, 923, 798 cm^{-1};

LRMS (ES/APCI) calcd for $C_{18}H_{20}ClFeN$ (M+H) 341.7, found 342.0.



4-Methylpyrindinyl-pentamethylcyclopentadienyliron (2). In a glove box, 4-chloropyrindinyl-pentamethylcyclopentadienyliron (150 mg, 0.44 mmol), methylboronic acid (32 mg, 0.53 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (51 mg, 0.044 mmol, 0.1 equiv), anhydrous K_2CO_3 (182 mg, 1.32 mmol, 3.0 equiv), and 1,4-dioxane (8 mL) were combined in a 20-mL vial. The vial was capped, sealed with electrical tape, removed from the glove box, and heated to 100 °C for 24 h. Next, the purple-brown mixture was allowed to cool to room temperature, and then it was passed through a plug of silica gel and washed with diethyl ether. The filtrate was concentrated under vacuum to yield a purple solid. The product was purified by flash chromatography (10% to 20% EtOAc/hexanes) on silica gel, which afforded the title compound as a purple solid: 131 mg (93% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, J = 4.2 Hz, 1H), 6.70 (d, J = 3.9 Hz, 1H), 4.72 (d, J = 2.1 Hz, 1H), 4.29 (d, J = 2.4 Hz, 1H), 3.88 (t, J = 2.4 Hz, 1H), 2.40 (s, 3H), 1.65 (s, 15H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.6, 150.8, 116.0, 109.0, 83.2, 78.3, 76.2, 67.3, 61.8, 19.6, 10.0;

LRMS (ES/APCI) calcd for $C_{19}H_{23}FeN$ (M^+) 321.2, found 321.9.

The enantiomers of catalyst **2** were separated by semi-preparative chiral HPLC: Daicel OD, 25 cm × 10 mm; diethylamine/EtOAc/hexanes (0.4 : 3 : 97); 0.8 mL/min flow rate; 25.0 mg catalyst in 0.5 mL solvent (hexanes/ether = 4/1) per injection.

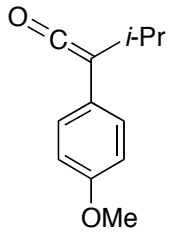
(+)-**2** ($[\alpha]_D^{25}$ = +730 (c = 0.0060, $CHCl_3$)) was collected from 55.0 min to 72.5 min.

(–)-**2** ($[\alpha]_D^{25}$ = –730 (c = 0.0060, $CHCl_3$)) was collected from 45.0 min to 51.2 min. The absolute configuration of (–)-**2** was determined by X-ray crystallography (see below).

III. Syntheses of Ketenes

Phenyl isopropyl ketene,[4] *p*-chlorophenyl isopropyl ketene,[4] 3-thienyl isopropyl ketene,[5] phenyl cyclohexyl ketene,[4] phenyl cyclopentyl ketene,[4] phenyl *t*-butyl ketene,[4] phenyl ethyl ketene,[6] *o*-tolyl ethyl ketene,[7] and *o*-methoxyphenyl methyl ketene[7] were synthesized according to literature procedures.

The following syntheses have not been optimized.

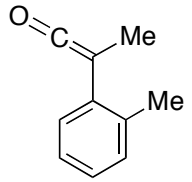


4-Methoxyphenyl isopropyl ketene. Me_2NEt (12.8 mL, 99.5 mmol) was added over 5 min to a 0 °C solution of 2-(4-methoxyphenyl)-3-methylbutanoyl chloride (4.50 g, 19.9 mmol) in THF (40 mL). The resulting mixture was stirred at room temperature for 14 h. Next, it was filtered under nitrogen and concentrated to a bright-yellow liquid, which was distilled (65 °C, 0.23 Torr) to yield 1.93 g (51%) of the desired ketene.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 3.79 (s, 3H), 2.81-2.66 (m, 1H), 1.20 (d, J = 6.9 Hz, 6H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 206.1, 157.2, 126.7, 123.9, 114.8, 55.5, 46.7, 30.5, 24.8, 22.3;

IR (neat) 2961, 2091, 1608, 1151, 1280, 1248, 1181, 1039, 825 cm^{-1}.



***o*-Tolyl methyl ketene.** Me_2NEt (14.1 mL, 110 mmol) was added over 5 min to a 0 °C solution of 2-*o*-tolylpropanoyl chloride (4.00 g, 21.9 mmol) in THF (40 mL). The resulting mixture was stirred at room temperature for 13 h. Next, it was filtered under nitrogen and concentrated to a bright-yellow liquid, which was distilled (43 °C, 0.41 Torr) to yield 2.07 g (64%) of the desired ketene.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.04 (m, 4H), 2.32 (s, 3H), 2.07 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 201.1, 134.8, 132.1, 130.6, 126.7, 125.4, 125.2, 30.9, 21.2, 12.0;

IR (neat) 2949, 2096, 1751, 1490, 1266, 1089, 756 cm^{-1}.

IV. Catalytic Enantioselective Addition of HN_3 to Ketenes

General Procedure A: (*R*)-Methyl 2-methyl-1-phenylpropylcarbamate (Table 1, entry 1). In a glove box, a solution of phenyl isopropyl ketene (48.0 mg, 0.30 mmol) in toluene (6 mL) and hexanes (1.5 mL) was prepared in a 25-mL one-necked flask. The flask was capped with a septum, removed from the glove box, and cooled to –78 °C. In the air, catalyst (–)-**2** (9.6 mg, 0.030 mmol, 10 mol%) was weighed into a vial, which was then sealed with a cap equipped with a Teflon septum and purged with argon. Toluene (1.0 mL) was added to the catalyst, and the resulting solution was added via syringe to the –78 °C solution of the ketene, resulting in a purple solution. In a glove box, HN_3 (0.90 M in CH_2Cl_2; 367 μL, 0.33 mmol, 1.1 equiv) was diluted with toluene (1.5 mL), transferred to a 3-mL syringe, and removed from the glove box. This solution of HN_3 was added by syringe pump over 1.0 h to the –78 °C solution of catalyst and ketene. After the addition was complete, the reaction mixture was stirred for an additional 5 h at –78 °C. Next, the dry ice-acetone bath was removed, and the reaction mixture was allowed to warm to room temperature over ~30 min. Benzene (3 mL) was added, and the resulting mixture was heated at 90 °C for 1 h. Next, MeOH (2 mL) was added, and the reaction mixture was heated at 75 °C for 12 h. The mixture was then allowed to cool to room temperature, and the solution was concentrated in vacuo. The residue was purified by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (57.0 mg, 92% yield).

[This reaction was also run on a 1.17 mmol scale, which provided the desired product in 84% yield (203 mg) and 94% ee.]

$[\alpha]_D^{23} = 69.5$ (c = 0.66, $CHCl_3$). HPLC analysis: 96% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 10.3 min (minor), 13.0 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: phenyl isopropyl ketene (18.7 mg, 0.12 mmol), (+)-**2** (3.7 mg, 0.012 mmol, 10 mol%), and HN_3 (1.7 M in CH_2Cl_2; 77 μL, 0.13 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (22.5 mg, 94% yield, 96% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.12 (m, 5H), 5.05 (br s, 1H), 4.38 (br t, J = 8.0 Hz, 1H), 3.56 (s, 3H), 1.95-1.89 (m, 1H), 0.88 (d, J = 6.5 Hz, 3H), 0.76 (d, J = 7.0 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 142.1, 128.6, 127.3, 126.9, 61.3, 52.3, 33.8, 19.9, 18.8;

IR (neat) 3291, 1689 (C=O), 1537, 1243, 1023, 699 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{12}H_{17}NO_2$ (M^+): 207, found 207.

(*R*)-Methyl 1-(4-chlorophenyl)-2-methylpropylcarbamate (Table 1, entry 2). General Procedure A was followed: *p*-chlorophenyl isopropyl ketene (59.0 mg, 0.30 mmol), (–)-**2** (9.6 mg, 0.030 mmol, 10 mol%), and HN_3 (2.0 M in CH_2Cl_2; 167 μL, 0.33 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (65.0 mg, 90% yield).

$[\alpha]_D^{23}$ = 65.9 (c = 1.85, $CHCl_3$). HPLC analysis: 93% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 12.4 min (minor), 15.3 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: *p*-chlorophenyl isopropyl ketene (50.0 mg, 0.26 mmol), (+)-**2** (8.4 mg, 0.026 mmol, 10 mol%), and HN_3 (1.2 M in CH_2Cl_2; 236 μL, 0.28 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (55.0 mg, 89% yield, 92% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.13 (m, 4H), 5.13 (br d, J = 13.0 Hz, 1H), 4.40 (br t, J = 13.0 Hz, 1H), 3.63 (s, 3H), 1.98-1.88 (m, 1H), 0.93 (d, J = 11.0 Hz, 3H), 0.81 (d, J = 11.0 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 140.7, 132.9, 128.7, 128.3, 60.8, 52.3, 33.6, 19.9, 18.7;

IR (neat) 3342, 2958, 1692 (C=O), 1536, 1256, 1030, 825 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{12}H_{16}ClNO_2$ (M^+): 241, found 241.

(*R*)-Methyl 1-(4-methoxyphenyl)-2-methylpropylcarbamate (Table 1, entry 3). General Procedure A was followed: *p*-methoxyphenyl isopropyl ketene (18.4 mg, 0.10 mmol), (–)-**2** (3.2 mg, 0.010 mmol, 10 mol%), and HN_3 (2.3 M in CH_2Cl_2; 46 μL, 0.11 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (21.6 mg, 95% yield).

$[\alpha]_D^{23}$ = 80.7 (c = 0.83, $CHCl_3$). HPLC analysis: >98% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 15.6 min (minor), 23.2 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: *p*-methoxyphenyl isopropyl ketene (53.0 mg, 0.28 mmol), (+)-**2** (9.0 mg, 0.028 mmol, 10 mol%), and HN_3 (1.1 M in CH_2Cl_2; 307 μL, 0.31 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (70.0 mg, 92% yield, 96% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.30 (br d, *J* = 9.0 Hz, 1H), 4.40 (br t, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 2.00-1.81 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 156.7, 134.2, 128.0, 113.9, 60.9, 55.4, 52.3, 33.8, 19.9, 19.0;

IR (neat) 3348, 2956, 1693 (C=O), 1537, 1299, 1258, 1025, 812 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{13}H_{19}NO_3$ (M^+): 237, found 237.

(*R*)-Methyl 2-methyl-1-(thiophen-3-yl)propylcarbamate (Table 1, entry 4). General Procedure A was followed: 3-thiophenyl isopropyl ketene (20.4 mg, 0.12 mmol), (–)-**2** (4.0 mg, 0.012 mmol, 10 mol%), and HN_3 (2.3 M in CH_2Cl_2; 59 μL, 0.14 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (24.2 mg, 93% yield).

$[\alpha]_D^{23}$ = 54.7 (c = 1.72, $CHCl_3$). HPLC analysis: 95% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 12.5 min (minor), 17.6 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: 3-thiophenyl isopropyl ketene (37.0 mg, 0.22 mmol), (+)-**2** (7.1 mg, 0.022 mmol, 10 mol%), and HN_3 (0.90 M in CH_2Cl_2; 272 μL, 0.25 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (43.0 mg, 91% yield, 94% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 5.0, 2.5 Hz, 1H), 7.07 (br s, 1H), 6.96 (br d, *J* = 5.0 Hz, 1H), 4.98 (br s, 1H), 4.64 (br t, *J* = 8.0 Hz, 1H), 3.67 (s, 3H), 2.09-2.02 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 143.0, 126.2, 126.1, 121.2, 57.1, 52.3, 33.5, 19.7, 18.4;

IR (neat) 3324, 2959, 1698 (C=O), 1539, 1244, 1029, 779 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{10}H_{15}NO_2S$ (M^+): 213, found 213.

(*R*)-Methyl cyclohexyl(phenyl)methylcarbamate (Table 1, entry 5). General Procedure A was followed: phenyl cyclohexyl ketene (62.0 mg, 0.31 mmol), (–)-**2** (9.9 mg, 0.031 mmol, 10 mol%), and HN_3 (2.3 M in CH_2Cl_2; 148 μL, 0.34 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on

silica gel, which afforded the desired methyl carbamate as a white solid (71.0 mg, 93% yield).

$[\alpha]_D^{23}$ = 54.0 (c = 1.64, $CHCl_3$). HPLC analysis: 96% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 13.4 min (minor), 14.9 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: phenyl cyclohexyl ketene (52.0 mg, 0.26 mmol), (+)-**2** (8.4 mg, 0.026 mmol, 10 mol%), and HN_3 (1.0 M in CH_2Cl_2; 286 μL, 0.29 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (58.0 mg, 91% yield, 96% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.18 (m, 5H), 5.13 (br s, 1H), 4.47 (br t, *J* = 8.5 Hz, 1H), 3.64 (s, 3H), 1.87 (br d, *J* = 13.0 Hz, 1H), 1.80-1.72 (m, 1H), 1.70-1.60 (m, 3H), 1.43 (br d, *J* = 13.0 Hz, 1H), 1.22-1.10 (m, 3H), 1.06-0.90 (m, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 142.0, 128.6, 127.2, 127.0, 60.7, 52.2, 43.5, 30.3, 29.4, 26.4, 26.21, 26.20;

IR (neat) 3366, 2938, 1692 (C=O), 1531, 1248, 1023, 759, 701 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{15}H_{21}NO_2$ (M^+): 247, found 247.

(*R*)-Methyl cyclopentyl(phenyl)methylcarbamate (Table 1, entry 6). General Procedure A was followed: phenyl cyclopentyl ketene (53.0 mg, 0.28 mmol), (–)-**2** (9.2 mg, 0.028 mmol, 10 mol%), and HN_3 (2.3 M in CH_2Cl_2; 136 μL, 0.31 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (62.0 mg, 94% yield).

$[\alpha]_D^{23}$ = 136 (c = 0.65, $CHCl_3$). HPLC analysis: 97% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 13.1 min (minor), 14.3 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: phenyl cyclopentyl ketene (50.0 mg, 0.27 mmol), (+)-**2** (8.7 mg, 0.027 mmol, 10 mol%), and HN_3 (1.1 M in CH_2Cl_2; 296 μL, 0.30 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (57.5 mg, 92% yield, 94% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.22 (m, 5H), 5.15 (br s, 1H), 4.46 (br t, *J* = 8.5 Hz, 1H), 3.63 (s, 3H), 2.26-2.18 (m, 1H), 1.88-1.80 (m, 1H), 1.74-1.40 (m, 6H), 1.20-1.12 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 143.0, 128.6, 127.3, 127.0, 60.2, 52.2, 46.0, 30.4, 30.1, 25.4;

IR (neat) 3362, 2945, 1693 (C=O), 1529, 1293, 1255, 1025, 700 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{14}H_{19}NO_2$ (M^+): 233, found 233.

(*R*)-Methyl 2,2-dimethyl-1-phenylpropylcarbamate (Table 1, entry 7). General Procedure A was followed: phenyl *t*-butyl ketene (46.0 mg, 0.26 mmol), (–)-**2** (8.5 mg,

0.026 mmol, 10 mol%), and HN_3 (1.5 M in CH_2Cl_2; 193 μL, 0.29 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (54.0 mg, 93% yield).

$[\alpha]_D^{23}$ = 39.2 (c = 0.68, $CHCl_3$). HPLC analysis: 79% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 8.9 min (minor), 11.2 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: phenyl *t*-butyl ketene (19.0 mg, 0.11 mmol), (+)-**2** (3.5 mg, 0.011 mmol, 10 mol%), and HN_3 (1.0 M in CH_2Cl_2; 120 μL, 0.12 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (22.5 mg, 94% yield, 74% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.16 (m, 5H), 5.31 (br s, 1H), 4.50 (d, *J* = 9.0 Hz, 1H), 3.63 (s, 3H), 0.92 (s, 9H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 140.5, 128.1, 128.0, 127.2, 64.1, 52.3, 35.1, 26.9;

IR (neat) 3336, 2955, 1699 (C=O), 1540, 1366, 1252, 1011, 706 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{13}H_{19}NO_2$ (M^+): 221, found 221.

General Procedure B. (*R*)-Methyl 1-*o*-tolylpropylcarbamate (Table 1, entry 9). Because higher ee's could be obtained at lower temperature, in certain cases the addition reactions were conducted at –90 °C, rather than at –78 °C.

In a glove box, a solution of *o*-tolyl ethyl ketene (19.4 mg, 0.121 mmol) in toluene (6.4 mL) and hexanes (1.6 mL) was prepared in a 25-mL one-necked flask. The flask was capped with a septum, removed from the glove box, and cooled to –90 °C. In the air, catalyst (–)-**2** (4.2 mg, 0.012 mmol, 10 mol%) was weighed into a vial, which was then sealed with a cap equipped with a Teflon septum and purged with argon. Toluene (0.4 mL) was added to the catalyst, and the resulting solution was added via syringe to the –90 °C solution of the ketene, resulting in a purple solution. In a glove box, HN_3 (2.3 M in CH_2Cl_2; 58 μL, 0.145 mmol, 1.1 equiv) was diluted with toluene (0.8 mL), transferred to a 3-mL syringe, and removed from the glove box. This solution of HN_3 was added by syringe pump over 2.0 h to the –90 °C solution of catalyst and ketene. After the addition was complete, the reaction mixture was stirred for an additional 4 h at –90 °C. Next, the reaction vessel was removed from the cooling bath and allowed to warm to room temperature over ~30 min. Benzene (3 mL) was added, and the resulting mixture was heated to reflux for 1 h. Next, MeOH (1.5 mL) was added, and the reaction mixture was refluxed for 12 h. The mixture was then allowed to cool to room temperature, and the solution was concentrated in vacuo. The residue was purified by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (23.5 mg, 94% yield).

$[\alpha]_D^{23}$ = 76.3 (c = 0.63, $CHCl_3$). HPLC analysis: 94% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 8.3 min (minor), 11.1 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: *o*-tolyl ethyl ketene (48.0 mg, 0.30 mmol), (+)-**2** (9.6 mg, 0.030 mmol, 10 mol%), and HN_3 (1.0 M in CH_2Cl_2; 330 μL, 0.33 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (57.0 mg, 92% yield, 94% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21-7.14 (m, 4H), 4.99 (br s, 1H), 4.90-4.78 (m, 1H), 3.65 (s, 3H), 2.42 (s, 3H), 1.82-1.69 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 141.0, 136.0, 130.8, 127.2, 126.5, 125.0, 52.9, 52.2, 29.5, 19.6, 11.0;

IR (neat) 3359, 2968, 1695 (C=O), 1531, 1240, 1026, 755, 710 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{12}H_{17}NO_2$ (M^+): 207, found 207.

(*R*)-Methyl 1-phenylpropylcarbamate (Table 1, entry 8). General Procedure B was followed: phenyl ethyl ketene (17.9 mg, 0.12 mmol), (–)-**2** (4.0 mg, 0.012 mmol, 10 mol%), and HN_3 (2.3 M in CH_2Cl_2; 59 μL, 0.15 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (21.2 mg, 90% yield).

HPLC analysis: 4% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 11.7 min (minor), 13.6 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: phenyl ethyl ketene (43.8 mg, 0.30 mmol), (+)-**2** (9.6 mg, 0.030 mmol, 10 mol%), and HN_3 (0.90 M in CH_2Cl_2; 367 μL, 0.33 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (51.0 mg, 88% yield, 5% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (m, 2H), 7.27-7.19 (m, 3H), 4.95-4.93 (m, 1H), 4.59-4.57 (m, 1H), 3.65 (s, 3H), 1.81-1.77 (m, 2H), 0.91 (dd, J = 7.4, 3.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 142.5, 128.3, 127.0, 126.2, 56.7, 51.8, 29.4, 10.6;

IR (neat) 3302, 2960, 1693 (C=O), 1542, 1304, 1260, 703 cm^{-1};

LRMS (ES/APCI) calcd for $C_{11}H_{15}NO_2$ (M+Na$^+$) 216.1, found 216.1.

(*R*)-Methyl 1-*o*-tolylethylcarbamate (Table 1, entry 10). General Procedure B was followed: *o*-tolyl methyl ketene (24.0 mg, 0.16 mmol), (–)-**2** (5.3 mg, 0.016 mmol, 10 mol%), and HN_3 (1.1 M in CH_2Cl_2; 164 μL, 0.18 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (29.0 mg, 91% yield).

$[\alpha]_D^{23}$ = 41.9 (c = 0.64, $CHCl_3$). HPLC analysis: 79% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 9.3 min (minor), 11.2 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: *o*-tolyl methyl ketene (42.0 mg, 0.29 mmol), (+)-**2** (9.3 mg, 0.029 mmol, 10 mol%), and HN_3 (1.0 M in CH_2Cl_2; 316 μL, 0.32 mmol, 1.1 equiv). The (*S*) product was isolated by flash

chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (49.0 mg, 89% yield, 82% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.15 (m, 4H), 5.10-4.95 (m, 2H), 3.66 (s, 3H), 2.41 (s, 3H), 1.46 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 141.7, 135.6, 130.8, 127.4, 126.5, 124.6, 52.2, 47.2, 21.9, 19.3;

IR (neat) 3329, 2930, 1695 (C=O), 1532, 1249, 1070, 759 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{11}H_{15}NO_2$ (M^+): 193, found 193.

(*R*)-Methyl 1-(4-methoxyphenyl)propylcarbamate (Table 1, entry 11). General Procedure B was followed: *p*-methoxyphenyl ethyl ketene (53.0 mg, 0.30 mmol), (–)-**2** (9.6 mg, 0.030 mmol, 10 mol%), and HN_3 (2.0 M in CH_2Cl_2; 167 μL, 0.33 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (62.0 mg, 93% yield).

$[\alpha]_D^{23}$ = 54.6 (c = 1.53, $CHCl_3$). HPLC analysis: 55% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 16.9 min (minor), 22.6 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: *p*-methoxyphenyl ethyl ketene (45.0 mg, 0.26 mmol), (+)-**2** (8.3 mg, 0.026 mmol, 10 mol%), and HN_3 (0.90 M in CH_2Cl_2; 312 μL, 0.28 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (51.0 mg, 90% yield, 55% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 14.0 Hz, 2H), 6.89-6.85 (m, 2H), 5.00 (br s, 1H), 4.55-4.48 (m, 1H), 3.79 (s, 3H), 3.64 (s, 3H), 1.86-1.69 (m, 2H), 0.89 (t, *J* = 12.0 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 156.6, 134.8, 127.7, 114.1, 56.5, 55.4, 52.2, 29.7, 10.9;

IR (neat) 3356, 2961, 1691 (C=O), 1528, 1238, 1030, 817 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{12}H_{17}NO_3$ (M^+): 223, found 223.

(*R*)-Methyl 1-(2-methoxyphenyl)ethylcarbamate (Table 1, entry 12). General Procedure B was followed: *o*-methoxyphenyl methyl ketene (53.0 mg, 0.32 mmol), (–)-**2** (10.2 mg, 0.032 mmol, 10 mol%), and HN_3 (2.0 M in CH_2Cl_2; 180 μL, 0.36 mmol, 1.1 equiv). The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (61.0 mg, 91% yield).

$[\alpha]_D^{23}$ = 95.4 (c = 0.58, $CHCl_3$). HPLC analysis: 70% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 12.0 min (minor), 14.4 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: *o*-methoxyphenyl methyl ketene (42.0 mg, 0.26 mmol), (+)-**2** (8.3 mg, 0.026 mmol, 10

mol%), and HN_3 (0.90 M in CH_2Cl_2; 317 μL, 0.29 mmol, 1.1 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a colorless oil (48.0 mg, 89% yield, 70% ee).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.19 (m, 2H), 6.95-6.87 (m, 2H), 5.58 (br s, 1H), 5.10-4.90 (m, 1H), 3.87 (s, 3H), 3.65 (s, 3H), 1.46 (d, *J* = 11.0 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 156.4, 131.4, 128.6, 127.9, 121.0, 111.1, 55.5, 52.1, 49.3, 21.9;

IR (neat) 3349, 2946, 1692 (C=O), 1534, 1242, 1073, 1027, 751, 700 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{11}H_{15}NO_3$ (M^+): 209, found 209.

(*R*)-Benzyl 2-methyl-1-phenylpropylcarbamate (Eq 4). General Procedure A was followed: phenyl isopropyl ketene (29.0 mg, 0.18 mmol), (–)-**2** (6.0 mg, 0.018 mmol, 10 mol%), and HN_3 (1.2 M in CH_2Cl_2; 166 μL, 0.20 mmol, 1.1 equiv). Instead of quenching the isocyanate with MeOH, benzyl alcohol (38 μL, 0.36 mmol, 2.0 equiv) was used. The product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (46.0 mg, 90% yield).

$[\alpha]_D^{23}$ = 28.6 (c = 0.48, $CHCl_3$). HPLC analysis: 95% ee [Daicel CHIRALPAK IA column; solvent system: 3% isopropanol/hexanes; 1.0 mL/min; retention times: 20.7 min (minor), 25.7 min (major)].

The second run was performed with the other enantiomer of catalyst **2**: phenyl isopropyl ketene (23.0 mg, 0.14 mmol), (+)-**2** (4.6 mg, 0.014 mmol, 10 mol%), HN_3 (1.3 M in CH_2Cl_2; 121 μL, 0.16 mmol, 1.1 equiv), and benzyl alcohol (30 μL, 0.28 mmol, 2.0 equiv). The (*S*) product was isolated by flash chromatography (5% to 10% EtOAc/hexanes) on silica gel, which afforded the desired methyl carbamate as a white solid (37.0 mg, 93% yield, 95% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.19 (m, 10H), 5.17 (br d, *J* = 7.5 Hz, 1H), 5.06 (dd, *J* = 22.8, 12.3 Hz, 2H), 4.48 (br t, *J* = 8.1 Hz, 1H), 2.03-1.86 (m, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 141.9, 136.6, 128.7, 128.6, 128.4, 127.3, 126.9, 67.0, 61.4, 33.9, 19.9, 18.8;

IR (neat) 3327, 2960, 1699 (C=O), 1539, 1235, 1023, 699 cm^{-1};

EIMS (70 eV) m/z: calcd for $C_{18}H_{21}NO_2$ (M^+): 283, found 283.

(*S*)-1-*o*-Tolylpropan-1-amine (Eq 5; assignment of the absolute configuration of the reaction products). In a glove box, a solution of *o*-tolyl ethyl ketene (57.0 mg, 0.35 mmol) in toluene (25 mL) and hexanes (5 mL) was prepared in a 50-mL one-necked flask. The flask was capped with a septum, removed from the glove box, and cooled to –90 °C. In the air, catalyst (+)-**2** (11.6 mg, 0.035 mmol, 10 mol%) was weighed into a vial, which was then sealed with a cap equipped with a Teflon septum and purged with argon. Toluene (1.0 mL) was added to the catalyst, and the resulting solution was added via syringe to the –90 °C solution of the ketene, resulting in a purple solution. In a glove box, HN_3 (1.1 M in CH_2Cl_2; 356 μL, 0.39 mmol, 1.1 equiv) was diluted with

toluene (1.5 mL), transferred to a 3-mL syringe, and removed from the glove box. This solution of HN_3 was added by syringe pump over 2.0 h to the –90 °C solution of catalyst and ketene. After the addition was complete, the reaction mixture was stirred for an additional 4 h at –90 °C. Next, the reaction vessel was removed from the cooling bath and allowed to warm to room temperature over ~30 min. Benzene (3 mL) was added, and the resulting mixture was heated to reflux for 1 h. The solvent was then removed, a solution of HCl (8 M; 20 mL) was added, and the reaction mixture was heated to reflux for 13 h. The mixture was neutralized with a 10% aqueous solution of NaOH and extracted with Et_2O. The organics layers were combined, washed with brine, dried (Na_2SO_4), filtered, and concentrated to dryness. The product was isolated by flash chromatography (1% to 5% MeOH/CH_2Cl_2) on silica gel, which afforded the desired primary amine as a pale-yellow oil (51.0 mg, 97% yield, 90% ee; the ee was determined by converting the amine into the methyl carbamate).

The spectral data of the amine are consistent with those reported in the literature.[8]

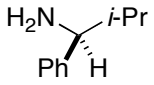
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 8.0 Hz, 1H), 7.24-7.19 (m, 1H), 7.14-7.12 (m, 2H), 4.09 (t, J = 7.0 Hz, 1H), 2.35 (s, 3H), 1.75-1.60 (m, 2H), 1.45 (br s, 2H), 0.92 (t, J = 7.5 Hz, 3H).

The spectral data of the amine are consistent with those reported in the literature.[9]

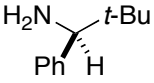
^{1}H NMR (500 MHz, CD_3OD): δ 7.47 (d, J = 7.5 Hz, 1H), 7.38-7.31 (m, 2H), 7.30 (d, J = 4.0 Hz, 1H), 4.52 (dd, J = 8.0, 6.0 Hz, 1H), 2.44 (s, 3H), 2.13-2.07 (m, 1H), 2.02-1.95 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H).

$[\alpha]_D^{23}$ = 12.0 (c = 0.60, CH_3OH). [lit.[9] $[\alpha]_D^{23}$ = 23.3 (c = 0.93, CD_3OD) for the (S) isomer]

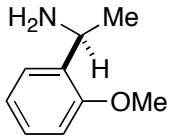
Confirmation of the assignment of the absolute configuration of the reaction products was obtained by hydrolysis of several of the products illustrated in Table 1.



(*S*)-2-Methyl-1-phenylpropan-1-amine. Produced by (+)-**2**. Pale-yellow oil. The ^{1}H NMR spectrum matched the previously reported data.[10] $[\alpha]_D^{23}$ = –9.1 (c = 0.60, $CHCl_3$). [lit.[10] $[\alpha]_D^{23}$ = –11.5 (c = 0.93, $CHCl_3$)]



(*S*)-2,2-Dimethyl-1-phenylpropan-1-amine. Produced by (+)-**2**. Pale-yellow oil. The ^{1}H NMR spectrum matched the previously reported data.[10] $[\alpha]_D^{23}$ = –2.9 (c = 1.1, $CHCl_3$). [lit.[10] $[\alpha]_D^{23}$ = –5.5 (c = 1.0, $CHCl_3$)]



(*S*)-1-(2-Methoxyphenyl)ethanamine. Produced by (+)-**2**. Pale-yellow oil. The ^{1}H NMR spectrum matched the previously reported data.[11] $[\alpha]_D^{23} = -9.9$ (c = 1.0, $CHCl_3$). [lit.[11] $[\alpha]_D^{23} = -18.8$ (c = 1.0, $CHCl_3$)]

V. Determination of the Absolute Configuration of (–)-2.

Crystals suitable for X-ray diffraction analysis were obtained by slowly evaporating a MeOH/H_2O solution of catalyst (–)-**2**.

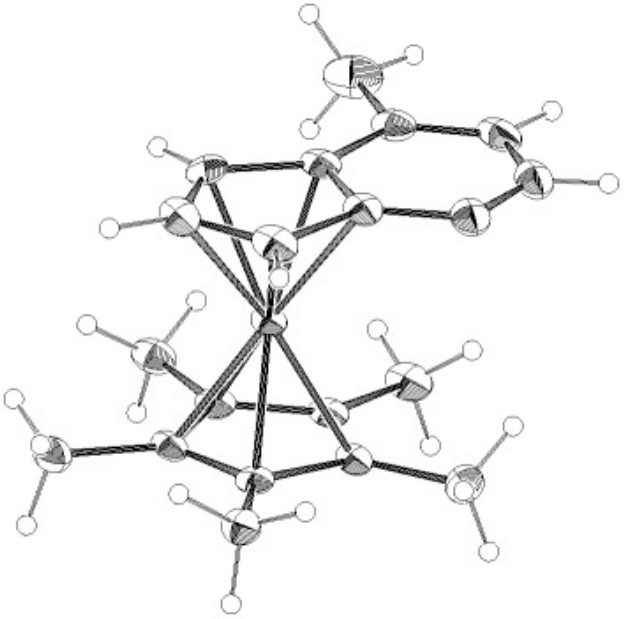


Table 1. Crystal data and structure refinement for catalyst (–)-**2**.

Identification code	07002	
Empirical formula	C19 H23 Fe N	
Formula weight	321.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.737(2) Å	α= 90°.
	b = 13.371(3) Å	β= 90°.
	c = 13.475(3) Å	γ = 90°.
Volume	1574.1(6) $Å^3$	
Z	4	
Density (calculated)	1.355 Mg/m^3	
Absorption coefficient	0.951 mm^{-1}	
F(000)	680	
Crystal size	0.45 x 0.30 x 0.01 mm^3	
Theta range for data collection	2.15 to 29.13°.	
Index ranges	-11<=h<=11, -18<=k<=18, -18<=l<=18	
Reflections collected	24224	
Independent reflections	4239 [R(int) = 0.0687]	
Completeness to theta = 29.13°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9906 and 0.6742	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4239 / 0 / 196	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0824	
R indices (all data)	R1 = 0.0698, wR2 = 0.0949	
Absolute structure parameter	-0.05(2)	
Largest diff. peak and hole	0.497 and -0.662 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Fe(1)	1164(1)	2432(1)	2132(1)	18(1)
C(1)	2907(4)	1538(2)	1633(2)	20(1)
C(2)	3515(2)	2422(2)	2091(2)	20(1)
C(3)	2926(4)	3276(2)	1581(2)	20(1)
C(4)	1956(4)	2918(2)	794(2)	19(1)
C(5)	1943(4)	1853(2)	825(2)	18(1)
C(6)	3267(4)	489(2)	1937(3)	27(1)
C(7)	4622(3)	2434(3)	2945(2)	30(1)
C(8)	3229(4)	4356(2)	1826(2)	26(1)
C(9)	1133(5)	3566(2)	54(2)	25(1)
C(10)	1034(4)	1191(2)	144(2)	24(1)
C(11)	1213(4)	891(2)	4476(2)	28(1)
C(12)	1750(4)	1811(3)	4866(2)	28(1)
C(13)	1383(3)	2708(2)	4441(2)	25(1)
C(14)	421(3)	2650(2)	3581(2)	21(1)
C(15)	-200(4)	3384(2)	2922(3)	26(1)
C(16)	-1074(4)	2867(2)	2192(3)	30(1)
C(17)	-958(4)	1822(3)	2362(2)	26(1)
C(18)	-45(4)	1681(3)	3235(2)	22(1)
C(19)	1887(5)	3701(3)	4831(3)	39(1)
N(1)	340(3)	793(2)	3685(2)	25(1)

Table 3. Bond lengths [Å] and angles [°] for catalyst (–)-**2**.

Fe(1)-C(4)	2.037(3)
Fe(1)-C(5)	2.039(3)
Fe(1)-C(16)	2.042(3)
Fe(1)-C(15)	2.044(3)
Fe(1)-C(1)	2.048(3)
Fe(1)-C(3)	2.049(3)
Fe(1)-C(17)	2.049(3)
Fe(1)-C(2)	2.055(2)
Fe(1)-C(14)	2.078(3)
Fe(1)-C(18)	2.081(3)
C(1)-C(2)	1.435(4)
C(1)-C(5)	1.440(4)
C(1)-C(6)	1.495(4)
C(2)-C(3)	1.428(4)
C(2)-C(7)	1.503(3)
C(3)-C(4)	1.439(4)
C(3)-C(8)	1.505(4)
C(4)-C(5)	1.424(4)
C(4)-C(9)	1.504(4)
C(5)-C(10)	1.503(4)
C(11)-N(1)	1.316(4)
C(11)-C(12)	1.417(5)
C(12)-C(13)	1.367(5)
C(13)-C(14)	1.434(4)
C(13)-C(19)	1.495(5)
C(14)-C(15)	1.431(4)
C(14)-C(18)	1.435(5)
C(15)-C(16)	1.425(5)
C(16)-C(17)	1.419(5)
C(17)-C(18)	1.434(4)
C(18)-N(1)	1.375(4)
C(4)-Fe(1)-C(5)	40.89(11)

C(4)-Fe(1)-C(16)	105.61(13)
C(5)-Fe(1)-C(16)	117.49(14)
C(4)-Fe(1)-C(15)	117.38(13)
C(5)-Fe(1)-C(15)	151.70(14)
C(16)-Fe(1)-C(15)	40.83(14)
C(4)-Fe(1)-C(1)	69.13(12)
C(5)-Fe(1)-C(1)	41.24(13)
C(16)-Fe(1)-C(1)	153.00(13)
C(15)-Fe(1)-C(1)	165.39(14)
C(4)-Fe(1)-C(3)	41.25(13)
C(5)-Fe(1)-C(3)	69.23(12)
C(16)-Fe(1)-C(3)	125.24(13)
C(15)-Fe(1)-C(3)	106.47(13)
C(1)-Fe(1)-C(3)	69.13(11)
C(4)-Fe(1)-C(17)	124.61(13)
C(5)-Fe(1)-C(17)	106.35(13)
C(16)-Fe(1)-C(17)	40.59(13)
C(15)-Fe(1)-C(17)	69.00(14)
C(1)-Fe(1)-C(17)	119.37(14)
C(3)-Fe(1)-C(17)	162.58(13)
C(4)-Fe(1)-C(2)	68.82(12)
C(5)-Fe(1)-C(2)	68.97(12)
C(16)-Fe(1)-C(2)	163.76(13)
C(15)-Fe(1)-C(2)	126.91(13)
C(1)-Fe(1)-C(2)	40.94(12)
C(3)-Fe(1)-C(2)	40.73(12)
C(17)-Fe(1)-C(2)	155.00(14)
C(4)-Fe(1)-C(14)	153.17(13)
C(5)-Fe(1)-C(14)	165.57(13)
C(16)-Fe(1)-C(14)	67.89(12)
C(15)-Fe(1)-C(14)	40.60(13)
C(1)-Fe(1)-C(14)	128.48(12)
C(3)-Fe(1)-C(14)	119.85(12)
C(17)-Fe(1)-C(14)	68.36(12)
C(2)-Fe(1)-C(14)	109.78(10)

C(4)-Fe(1)-C(18)	163.35(13)
C(5)-Fe(1)-C(18)	127.10(14)
C(16)-Fe(1)-C(18)	67.84(13)
C(15)-Fe(1)-C(18)	68.42(13)
C(1)-Fe(1)-C(18)	109.31(13)
C(3)-Fe(1)-C(18)	154.96(13)
C(17)-Fe(1)-C(18)	40.62(12)
C(2)-Fe(1)-C(18)	121.59(12)
C(14)-Fe(1)-C(18)	40.38(13)
C(2)-C(1)-C(5)	107.5(3)
C(2)-C(1)-C(6)	125.3(3)
C(5)-C(1)-C(6)	127.2(3)
C(2)-C(1)-Fe(1)	69.77(16)
C(5)-C(1)-Fe(1)	69.03(18)
C(6)-C(1)-Fe(1)	127.9(2)
C(3)-C(2)-C(1)	108.6(2)
C(3)-C(2)-C(7)	126.3(3)
C(1)-C(2)-C(7)	125.1(3)
C(3)-C(2)-Fe(1)	69.39(16)
C(1)-C(2)-Fe(1)	69.29(16)
C(7)-C(2)-Fe(1)	128.48(17)
C(2)-C(3)-C(4)	107.5(3)
C(2)-C(3)-C(8)	126.7(3)
C(4)-C(3)-C(8)	125.7(3)
C(2)-C(3)-Fe(1)	69.87(15)
C(4)-C(3)-Fe(1)	68.95(17)
C(8)-C(3)-Fe(1)	125.5(2)
C(5)-C(4)-C(3)	108.4(3)
C(5)-C(4)-C(9)	126.3(3)
C(3)-C(4)-C(9)	125.3(3)
C(5)-C(4)-Fe(1)	69.6(2)
C(3)-C(4)-Fe(1)	69.80(18)
C(9)-C(4)-Fe(1)	127.5(2)
C(4)-C(5)-C(1)	108.1(3)
C(4)-C(5)-C(10)	125.1(3)

C(1)-C(5)-C(10)	126.8(3)
C(4)-C(5)-Fe(1)	69.5(2)
C(1)-C(5)-Fe(1)	69.73(18)
C(10)-C(5)-Fe(1)	125.1(2)
N(1)-C(11)-C(12)	125.3(3)
C(13)-C(12)-C(11)	121.9(3)
C(12)-C(13)-C(14)	115.4(3)
C(12)-C(13)-C(19)	124.3(3)
C(14)-C(13)-C(19)	120.3(3)
C(15)-C(14)-C(13)	133.4(3)
C(15)-C(14)-C(18)	108.1(3)
C(13)-C(14)-C(18)	118.5(3)
C(15)-C(14)-Fe(1)	68.42(17)
C(13)-C(14)-Fe(1)	125.75(19)
C(18)-C(14)-Fe(1)	69.92(16)
C(16)-C(15)-C(14)	107.3(3)
C(16)-C(15)-Fe(1)	69.50(19)
C(14)-C(15)-Fe(1)	70.98(16)
C(17)-C(16)-C(15)	109.2(3)
C(17)-C(16)-Fe(1)	70.0(2)
C(15)-C(16)-Fe(1)	69.67(18)
C(16)-C(17)-C(18)	107.5(3)
C(16)-C(17)-Fe(1)	69.4(2)
C(18)-C(17)-Fe(1)	70.89(18)
N(1)-C(18)-C(17)	127.7(3)
N(1)-C(18)-C(14)	124.5(3)
C(17)-C(18)-C(14)	107.8(3)
N(1)-C(18)-Fe(1)	127.4(2)
C(17)-C(18)-Fe(1)	68.49(18)
C(14)-C(18)-Fe(1)	69.70(17)
C(11)-N(1)-C(18)	114.4(3)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	5(1)	33(1)	15(1)	2(1)	0(1)	1(1)
C(1)	7(2)	35(2)	16(2)	3(1)	0(1)	0(1)
C(2)	6(1)	38(2)	17(1)	1(2)	3(1)	0(1)
C(3)	7(2)	32(2)	22(2)	0(1)	5(1)	-2(1)
C(4)	10(2)	34(2)	14(2)	4(1)	2(1)	0(1)
C(5)	8(2)	29(2)	18(2)	-2(1)	3(1)	0(1)
C(6)	17(2)	35(2)	29(2)	4(1)	2(1)	5(1)
C(7)	9(1)	56(2)	24(1)	1(2)	-1(1)	2(2)
C(8)	19(2)	37(2)	22(2)	-1(1)	3(1)	-5(1)
C(9)	20(2)	35(2)	21(2)	3(1)	2(2)	3(2)
C(10)	14(2)	34(2)	23(2)	-1(1)	-2(1)	1(2)
C(11)	18(2)	42(2)	25(2)	10(1)	4(1)	4(2)
C(12)	17(2)	52(2)	15(2)	1(2)	0(1)	3(2)
C(13)	15(1)	40(2)	19(1)	-4(1)	2(1)	1(1)
C(14)	8(1)	37(2)	18(1)	0(1)	4(1)	0(1)
C(15)	13(2)	34(2)	30(2)	2(2)	11(2)	7(1)
C(16)	8(1)	57(2)	25(2)	10(2)	2(1)	7(1)
C(17)	7(2)	50(2)	23(2)	2(1)	1(1)	-3(1)
C(18)	9(2)	34(2)	22(2)	4(1)	5(1)	-1(1)
C(19)	34(2)	50(2)	33(2)	-15(2)	0(2)	-8(2)
N(1)	17(1)	33(2)	26(1)	5(1)	5(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for catalyst (–)-**2**.

	x	y	z	U(eq)
H(6A)	4259	292	1659	40
H(6B)	2469	39	1688	40
H(6C)	3309	448	2663	40
H(7A)	5661	2316	2697	44
H(7B)	4348	1907	3418	44
H(7C)	4579	3085	3277	44
H(8A)	3412	4424	2540	39
H(8B)	2339	4760	1637	39
H(8C)	4131	4587	1460	39
H(9A)	1771	3650	-538	38
H(9B)	928	4222	350	38
H(9C)	163	3249	-131	38
H(10A)	76	1526	-37	35
H(10B)	803	559	481	35
H(10C)	1630	1055	-457	35
H(11)	1506	297	4812	34
H(12)	2384	1804	5438	34
H(15)	-56	4087	2964	31
H(16)	-1644	3172	1673	36
H(17)	-1404	1309	1968	32
H(19A)	2532	3602	5418	59
H(19B)	988	4099	5012	59
H(19C)	2473	4053	4319	59

VI. References

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