Supplementary Information for:

# Highly Efficient Iridium-Catalyzed Asymmetric Hydrogenation

# of $\beta$ -Acylamino Nitroolefins

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### **1. Experimental Section**

**General Information:** All the air or moisture sensitive reactions and manipulations were performed by using standard Schlenk techniques and in anitrogen-filled glovebox. DME, Et<sub>2</sub>O, THF, dioxane and toluene were distilled from sodium benzophenoneketyl. CH<sub>2</sub>Cl<sub>2</sub> was distilled from calcium hydride. Anhydrous MeOH was distilled from magnesium. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AV (400 MHz) spectrometers. CDC1<sub>3</sub> or DMSO- $d_6$  was the solvent used for the NMR analysis, with tetramethylsilane as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for <sup>1</sup>H NMR. Optical rotation was determined using a Perkin Elmer 241 MC polarimeter. GC analysis was conducted on an Agilent 7890A Series instrument. HPLC analysis was conducted on an Agilent

1260 Series instrument. HRMS were recorded on a mass spectrometer with MALDI.



2. Preparation and Physical Data for (R, R)-f-spiroPhos<sup>[1, 2, 3]</sup>

1,1'-Bis(phosphine)ferrocene (394.0mg, 1.58mmol) was added to a solution of (*R*)-7,7'-dichloromethyl-1,1'-spirobiindane (1.0 g, 3.15mmol) and NaH (60%, 1.0 g, 24.78 mmol) in THF (38 mL) at -78°C under nitrogen. The mixture was stirred at room temperature for 24 h, and then heated at reflux for 17 h (monitored by <sup>31</sup>P NMR spectroscopy). After additional 1,1'-Bis(phosphine)ferrocene (50.0 mg, 0.20 mmol) was added, the mixture was stirred at reflux for another 25 h. After the reaction was completed (monitored by <sup>31</sup>P NMR spectroscopy), the solvent was removed under vacuum, and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was filtered through a silica-gel plug to give the yellow solid (600.0 mg, 52%). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +172.5 (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.25 (s, 1H), 7.19-7.17 (m, 3H), 7.11-7.10 (m, 2H), 6.99-6.97 (d, *J*= 7.32 Hz, 2H), 6.78-6.74 (t, *J*= 7.44 Hz, 2H), 5.84-5.82 (d, *J*= 7.48 Hz, 2H), 4.29 (s, 4H), 4.05 (s, 2H), 3.13 (s, 2H), 3.04-2.94(m, 4H), 2.93-2.80 (m, 10H), 2.36-2.29 (dd, *J*= 13.76, 7.84Hz, 2H), 2.27-2.22 (m, dd, *J*= 12.12, 6.52Hz, 2H), 2.19-2.14 (dd, J= 12.24, 6.56Hz, 2H), 1.98-1.81 (m, 4H) ;<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 147.7, 146.5, 142.9, 142.2, 133.0, 130.0, 129.6, 129.0, 128.4, 127.4, 126.0, 122.6, 121.9, 71.4, 70.5, 70.4, 61.2, 38.8, 38.5, 37.5, 30.6, 30.4, 27.4, 26.3; <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>)  $\delta$  = -28.74. MALDI-HRMS Calculated for C<sub>48</sub>H<sub>45</sub>FeP<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>): 739.2340, found 739.2342.

### **3.** General procedure for the synthesis of compound **3**<sup>[4]</sup>



Benzaldehyde (30.00 mmol), was added to a stirred solution of ammonium acetate (0.58 g, 7.50 mmol) in dry nitromethane (50 mL) at 90°C. The mixture was heated at reflux for 5 h, poured into water and extracted with diethyl ether ( $3 \times 50$  mL). The extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by recrystallization from ethanol to give the nitrostyrene **3** as light yellow solid.

## 4. General procedure for the synthesis of compound 1<sup>[5,6]</sup>



Triethylamine (4.3 mL, 0.03 mol) was added to a solution of methoxylamine-HCl (2.67 g, 0.03 mol) in dimethylformamide (50 mL) at 0 °C in an ice bath.  $\beta$ -Nitrostyrene **3** (0.03 mol) was added and stirred at 0 °C for 15 min then at rt for 5 min. Remove the precipate by filtration and wash the solid with a small amout of DMF. Place the combined filtrate into an addition funnel and add dropwise over 30 min to potassium *t*-butoxide (6.72 g, 0.06 mol) in DMF (80 mL) at 0 °C. Remove the bath and stir at rt for 30 min. Quench reaction with sat. NH<sub>4</sub>Cl (30 mL). Reaction volume reduced in 1/2 in vacuo and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Wash with water, brine, and dried

over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filter and concentrate in vacuo to give the desired material **4**. To a solution of **4** and DMAP (1.19 g, 0.01 mol) in 130 mL of  $CH_2Cl_2$  were added pyridine (16.6 mL, 2.0 eq, 0.12 mol) and Ac<sub>2</sub>O (8.90 mL, 0.09 mol) at 0°C. The resultant solution was warmed to rt and then stirred for 5 h. The reaction mixture was diluted with  $CH_2Cl_2$  and washed subsequently with water, and brine. After the solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, it was concentrated under vacuum, the residue was purification by flash chromatography on SiO<sub>2</sub> (PE/EA = 1:2) gave **1** as solid (**1r** as liquid).

#### 5. NMR and HRMS data of compound 1





(Z)-N-(1-(4-fluorophenyl)-2-nitrovinyl)acetamide 1b



Light yellow solid; Yield: 52%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ = 10.80 (s, 1H), 7.40-7.37 (m, 2H), 7.14-7.10 (m, 2H), 6.67 (s, 1H), 2.26 (s, 3H).<sup>[7]</sup>

(Z)-N-(1-(4-chlorophenyl)-2-nitrovinyl)acetamide 1c



Br

Light yellow solid; Yield: 65%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ =10.79 (s, 1H), 7.42-7.39 (m, 2H), 7.34-7.31 (m, 2H), 6.67 (s, 1H), 2.27 (s,3H).<sup>[7]</sup>

(Z)-N-(1-(4-bromophenyl)-2-nitrovinyl)acetamide 1d



(Z)-N-(1-(4-methoxyphenyl)-2-nitrovinyl)acetamide 1e



(Z)-N-(2-nitro-1-p-tolylvinyl)acetamide 1f



Light yellow solid; Yield: 86%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.79 (s, 1H), 7.29-7.26 (m, 2H), 7.24-7.22 (m, 2H), 6.71 (s, 1H), 2.40 (s, 3H), 2.24 (s, 3H).<sup>[7]</sup>

(Z)-N-(1-(4-trifluoromethylphenyl)-2-nitrovinyl)acetamide 1g



Light yellow solid; Yield: 34%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 10.82$  (s, 1H), 7.70-7.68 (d, J = 8.2, 2H), 7.51-7.49 (d, J =8.2, 2H), 6.66 (s, 1H), 2.28 (s, 3H); <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )  $\delta = 167.9, 147.8, 135.5, 132.6 (q, J = 32.7 Hz), 127.9,$ 

125.6 (q, J = 3.6 Hz), 123.6 (q, J = 271 Hz), 121.5, 25.0. MALDI-HRMS Calculated for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>KN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 313.0197, found 313.0193.

(Z)-N-(1-(3-fluorophenyl)-2-nitrovinyl)acetamide 1h



Light yellow solid; Yield: 67%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta =$ 10.68 (s, 1H), 7.36-7.31 (m, 1H), 7.14-7.09 (m, 2H), 7.03-7.00 (m, 1H), 6.61 (s, 1H), 2.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.9, 162.4 (d, J = 246.2 Hz), 147.9 (d, J = 2.2 Hz), 134.0 (d, J =8.2 Hz ), 130.3(d, J = 8.3 Hz), 123.3 (d, J = 3.2 Hz), 121.4, 117.8 (d, J = 21.0 Hz),

114.8 (d, J = 23.4 Hz), 25.0. MALDI-HRMS Calculated for C<sub>10</sub>H<sub>9</sub>FKN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 263.0229, found 263.0230.

(Z)-N-(1-(3-chlorophenyl)-2-nitrovinyl)acetamide 1i



(Z)-N-(2-nitro-1-m-tolylvinyl)acetamide1j



Light yellow solid; Yield: 64%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.78 (s, 1H), 7.32-7.30 (m, 2H), 7.19 (m, 1H), 6.69 (s, 1H), 2.39 (s, 3H), 2.25 (s, 3H).<sup>[7]</sup>

(Z)-N-(1-(3-methoxyphenyl)-2-nitrovinyl)acetamide 1k



Light yellow solid; Yield: 51%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.76 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.89 (s, 1H), 6.71 (s, 1H), 3.83 (s, 3H), 2.25(s, 3H).<sup>[7]</sup>

(Z/E)-N-(1-(2-fluorophenyl)-2-nitrovinyl)acetamide11

Light yellow solid; Yield: 62%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 11.00 (s, 1H), 8.72 (s,1H) 7.52-7.44 (m, 2H), 7.32-7.27 (m, 3H), 7.23-7.16 (m, 2H) 7.12-7.08 (m, 2H), 6.73 (s, 1H), 6.61 (s, 1H) 2.25 (s, 3H), 2.19 (s,1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) = 168.8,

160.3, 157.8, 139.4, 132.3 (d, J = 8.2 Hz), 128.9 (d, J = 1.9 Hz), 128.2, 124.8 (d, J = 3.6 Hz), 121.5 (d, J = 15.5), 116.3 (d, J = 21.2 Hz), 24.8. MALDI-HRMS Calculated for C<sub>10</sub>H<sub>9</sub>FKN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 263.0229, found 263.0230.

(Z)-N-(1-(2-chlorophenyl)-2-nitrovinyl)acetamide 1m



Light yellow solid; Yield: 84%; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$ = 10.44(s, 1H), 8.44 (s, 1H) 7.57-7.42 (m, 4H), 2.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.8, 142.5, 132.9, 132.2, 131.2, 130.1, 129.0, 127.9, 127.4, 24.7. MALDI-HRMS Calculated for

 $C_{10}H_9ClKN_2O_3^+$  ([M+K]<sup>+</sup>): 278.9933, found 278.9948.

(Z/E)-N-(2-nitro-1-o-tolylvinyl)acetamide1n



Light yellow solid; Yield: 79%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 11.2 (s, 1H), 8.73 (s, 1H), 7.39-7.33 (m, 2H), 7.31-7.26 (m, 2H), 7.24-7.21 (m, 2H), 7.17-7.14 (m, 2H), 6.68 (s, 1H), 6.49 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 2.25 (s, 3H); <sup>13</sup>C NMR (100

MHz, DMSO- $d_6$ )  $\delta$  = 171.5, 148.4, 135.6, 133.9, 130.4, 129.6, 127.9, 126.4, 125.6, 24.7, 19.1. MALDI-HRMS Calculated for C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>): 221.0921, found 221.0926.

(Z)-N-(1-(naphthalen-1-yl)-2-nitrovinyl)acetamide 10

$$\begin{array}{c} \bullet \\ \mathsf{HN} \\ \mathsf{(s, 1H), 7.98-7.92} \\ \mathsf{(m, 2H), 7.80-7.78} \\ \mathsf{(m, 1H), 7.58-7.51} \\ \mathsf{(m, 3H), 7.41-7.40} \\ \mathsf{(m, 1H), 6.82} \\ \mathsf{(s, 1H), 2.14} \\ \mathsf{(s, 3H); ^{13}C} \\ \mathsf{NMR} \\ \mathsf{(100 MHz, CDCl_3)} \\ \mathsf{\delta} = 168.8, 144.1, 133.5, 131.5, 130.3, 129.9, 128.8, 128.3, \\ \mathsf{HN} \\$$

127.7, 126.8, 125.4, 125.3, 123.7, 24.8. MALDI-HRMS Calculated for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>): 257.0921, found 257.0915.

(Z)-N-(1-(naphthalen-2-yl)-2-nitrovinyl)acetamide 1p



Light yellow solid; Yield: 85%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 10.90$  (s, 1H), 7.89-7.85 (m, 4H), 7.59-7.52 (m, 2H), 7.42 (dd, J = 8.5, 1.8 Hz, 1H), 6.82 (s, 1H), 2.28 (s, 3H).<sup>[7]</sup>

(Z)-N-(1-furyl-2-nitrovinyl)acetamide1q



Light yellow solid; Yield: 80%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.46 (s, 1H), 7.56 (m, 1H), 7.11 (s, 1H), 6.96 (d, *J* = 3.5, 1H), 6.54 (m, 1H) 2.28(s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.1, 146.2, 144.2, 137.4, 119.7, 117.6, 112.7, 25.0. MALDI-HRMS Calculated

for  $C_8H_9N_2O_4^+$  ([M+H]<sup>+</sup>): 197.0557, found 197.0553.

(Z)-N-(1-nitropent-1-en-2-yl)acetamide 1r

Light yellow liquid; Yield: 25%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 11.20 (s, 1H), 6.48 (s, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.18 (s, 3H), 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.92 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, 1.59-1.50 (m, 2H) 0.51 (t, J = 7.5) (

CDCl<sub>3</sub>)  $\delta$  = 168.4, 153.8, 118.1, 33.6, 25.6, 21.6, 13.9. MALDI-HRMS Calculated for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>): 173.0921, found 173.0926.

To a mixture of butyraldehyde (0.14 mol) and nitromethane (0.14 mol) in methanol 30 mL at 0 °C, a solution of NaOH (0.16 mol) in  $H_2O$  (6 mL) was added dropwise.

Further methanol (10 mL) was added and the resulting yellow slurry stirred at 0 °C for 3 h. Water (30 mL) was added and the clear yellow solution was poured into hydrochloric acid (60 mL conc. hydrochloric acid in 90 mL H<sub>2</sub>O) and stirred for 15 min. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL). The extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (PE/EA = 20:1) gave product **3r** as a yellow liquid (6.0 g, 38%).<sup>[8]</sup>

Triethylamine (5.8 mL, 41.6 mmol) was added to a solution of methoxylamine-HCl (3.6 g, 43.4 mmol) in dimethylformamide (70 mL) at 0 °C in an ice bath.  $\beta$ -Nitrostyrene 3r (34.7 mmol) was added and stirred at 0 °C for 1h then at rt for 1h. Remove the precipate by filtration and wash the solid with a small amout of DMF. Place the combined filtrate into an addition funnel and add dropwise about 50 min to potassium t-butyloxide (7.8 g, 69.4 mmol) in DMF (110 mL) at 0 °C. Remove the bath and stir at rt for 30 min. Quench reaction with sat. NH<sub>4</sub>Cl (40 mL). Reaction volume reduced in 1/2 in vacuo and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water, brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo to give the desired material 4r. To a solution of 4r and DMAP (1.39 g, 11.6 mmol) in 120 mL of CH<sub>2</sub>Cl<sub>2</sub> were added pyridine (11.5 mL, 4.0 eq, 138.8 mmol) and Ac<sub>2</sub>O (11.3 mL, 120.0 mmol) at 0 °C. The resultant solution was warmed to r.t. and then stirred for 4 h. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed subsequently with water, and brine. After the solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, it was concentrated under vacuum, the residue was purification by flash chromatography on SiO<sub>2</sub> (PE/EA = 1:5) gave 1r as light yellow liquid (1.2 g, 25%).<sup>[5,6]</sup> (Z)-N-(3-methyl-1-nitrobut-1-en-2-yl)acetamide 1s

 $\begin{array}{c} O \\ HN \\ \hline \\ NO_2 \end{array}$ Light yellow solid; Yield: 68%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 11.36$  (s, 1H), 6.61 (s, 1H), 4.03-3.93 (m, 1H), 2.22 (s, 3H), 1.15-1.13 (m, 6H).<sup>[7]</sup>

Isobutyraldehyde (80 mmol), was added to a stirred solution of ammonium acetate (1.6 g, 20 mmol) in dry nitromethane (130 mL) at 90°C. The

mixture was heated at reflux for 6 h, poured into water and extracted with diethyl ether (3 × 100 mL). The extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on SiO<sub>2</sub> (PE/EA = 1:20) gave **3s** as yellow liquid (4.2g, 44%).<sup>[4]</sup>

Triethylamine (6.1 mL, 43.7 mmol) was added to a solution of methoxylamine-HCl (3.8 g, 45.5 mmol) in dimethylformamide (70 mL) at 0 °C in an ice bath.  $\beta$ -Nitrostyrene 3s (36.4 mmol) was added and stirred at 0 °C for 1h then at rt for 1h. Remove the precipate by filtration and wash the solid with a small amout of DMF. Place the combined filtrate into an addition funnel and add dropwise about 50 min to potassium t-butoxide (8.2 g, 72.8 mmol) in DMF (110 mL) at 0 °C. Remove the bath and stir at rt for 30 min. Quench reaction with sat. NH<sub>4</sub>Cl (40 mL). Reaction volume reduced in 1/2 in vacuo and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Wash with water, brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filter and concentrate in vacuo to give the desired material 4s. To a solution of 4s and DMAP (1.5 g, 12.1 mmol) in 130 mL of CH<sub>2</sub>Cl<sub>2</sub> were added pyridine (12.0 mL, 4.0 eq, 145.6 mmol) and Ac<sub>2</sub>O (10.3 mL, 109 mmol) at 0 °C. The resultant solution was warmed to rt and then stirred for 12 h. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed subsequently with water, and brine. After the solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, it was concentrated under vacuum, the residue was purification by flash chromatography on SiO<sub>2</sub> (PE/EA = 1:5) gave 1s as light yellow solid (4.3 g, 68%).<sup>[5,6]</sup>

(Z)-N-(1-cyclohexyl-2-nitrovinyl)acetamide1t



Cyclohexanecarbaldehyde (50 mol), was added to a stirred solution of ammonium acetate (1.0 g, 13.4 mmol) in dry nitromethane (80 mL) at 90°C. The mixture was heated at reflux for 6 h, poured into water and extracted with diethyl ether (3  $\times$  50 mL). The extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated

under reduced pressure. The residue was purified by flash chromatography on  $SiO_2$  (PE/EA = 1:20) gave **3t** as light yellow liquid (5.3g, 64%).<sup>[4]</sup>

Triethylamine (5.7 mL, 41 mmol) was added to a solution of methoxylamine-HCl (3.6 g, 42.6 mmol) in dimethylformamide (70 mL) at 0 °C in an ice bath.  $\beta$ -Nitrostyrene **3t** (34.1 mmol) was added and stirred at 0 °C for 1h then at rt for 1h. Remove the precipate by filtration and wash the solid with a small amout of DMF. Place the combined filtrate into an addition funnel and add dropwise over 30 min to potassium t-butoxide (7.6 g, 68.2 mmol) in DMF (100 mL) at 0 °C. Remove the bath and stir at rt for 2h. Quench reaction with sat. NH<sub>4</sub>Cl (35 mL). Reaction volume reduced in 1/2 in vacuo and extracted with  $CH_2Cl_2$ . The organic phase was washed subsequently with water, brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to give the desired material 4t. To a solution of 4t and DMAP (0.8 g, 6.8 mmol) in 110 mL of CH<sub>2</sub>Cl<sub>2</sub> were added pyridine (11.3 mL, 4.0 eq, 136.4 mmol) and Ac<sub>2</sub>O (9.7 mL, 102.3 mmol) at 0 °C. The resultant solution was warmed to rt and then stirred for 5 h. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed subsequently with water, and brine. After the solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, it was concentrated under vacuum, the residue was purification by flash chromatography on SiO<sub>2</sub> (PE/EA = 1:6) gave 1t as light yellow solid (5.5g, 76%).<sup>[5,6]</sup>

#### 6. General Procedure for Asymmetric Hydrogenation of compound 1

A 20.0 mL vial was loaded with  $[Ir(COD)Cl]_2$  (2.1 mg, 0.003 mmol) and (*S*,*S*)-f-Binaphane (5.1 mg, 0.006 mmol). The mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (6.0 mL) and stirred for 20 min at room temperature in a nitrogen-filled glovebox. An aliquot of the catalyst solution (1.0 mL, 0.001 mmol) was transferred by syringe into the vials charged with different substrates (0.1 mmol for each) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (2.0 ml). The vials were then placed into a steel autoclave. The inert atmosphere was replaced by H<sub>2</sub> and the reaction mixture was stirred under H<sub>2</sub> (20 atm) at 80°C for 12 h. The hydrogen gas was released slowly and carefully. The solution was concentrated and passed through a short column of silica gel to remove the metal complex. The ee values of all compounds **2** were determined by GC or HPLC analysis on a chiral stationary phase.

#### 7. NMR, GC, HPLC, optical rotation and HRMS Data of compound 2

N-(2-nitro-1-phenylethyl)acetamide 2a

White solid; 99% ee;  $[\alpha]_D{}^{20} = -69.20$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 21.9 min (major), t<sub>R</sub> = 23.3 min (minor). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41-7.29 (m, 5H), 6.23 (d, *J* = 5.8 Hz, 1H), 5.70-5.65 (m, 1H), 4.93 (dd, *J* = 13.0, 6.3 Hz, 1H), 4.74 (dd, *J* = 13.0, 5.6 Hz, 1H), 2.07 (s, 3H). <sup>[9]</sup>

N-(1-(4-fluorophenyl)-2-nitroethyl)acetamide 2b



White solid; 99% ee;  $[\alpha]_D^{20} = -63.50$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 26.3 min (major), t<sub>R</sub> = 30.4 min (minor).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.31-7.28 (m, 2H), 7.10-7.05 (m, 2H), 6. 24 (d, *J* = 6.2 Hz, 1H), 5.64 (m, 1H), 4.91 (dd, *J* = 13.0, 6.2 Hz, 1H), 4.71 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.06 (s, 3H). <sup>[7]</sup>

*N*-(1-(4-chlorophenyl)-2-nitroethyl)acetamide 2c



White solid; >99.9% ee;  $[\alpha]_D{}^{20} = -76.30$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub>8.0 mL/min, programmed from 120 °C to 190 °C at 15.0 °C/min; t<sub>R</sub> = 28.0 min (major), t<sub>R</sub> = 35.9 min

(minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.29 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 9.9 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 1H), 5.60-5.55 (m, 1H), 4.82 (dd, *J* = 13.1, 6.4Hz, 1H), 4.65 (dd, *J* = 13.1, 5.3 Hz, 1H), 1.99 (s, 3H). <sup>[7]</sup>

N-(1-(4-bromophenyl)-2-nitroethyl)acetamide 2d

White solid; >99.9%ee; 
$$[\alpha]_D^{20} = -74.40$$
 (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC  
S11

condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25  $\mu$ m), N<sub>2</sub> 8.0 mL/min, programmed from 120 °C to 190 °C at 15.0 °C/min; t<sub>R</sub> = 41.7 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.52 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.30 (d, *J* = 7.2 Hz, 1H), 5.65-5.60 (m, 1H), 4.90 (dd, *J* = 13.1, 6.2 Hz, 1H), 4.72 (dd, *J* = 13.1, 5.3 Hz, 1H), 2.07 (s, 3H). <sup>[10]</sup>

*N*-(1-(4-methoxyphenyl)-2-nitroethyl)acetamide 2e

White solid; 99.3 HN  $NO_2$   $mm \times 0.25 \ \mu m$ ),  $100 \ \% \ ct \ 8 \ 0.90$ 

White solid; 99.3% ee;  $[\alpha]_D{}^{20} = -85.70$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 46.3 min (major), t<sub>R</sub> = 49.4 min

(minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.22 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.28 (d, *J* = 6.4 Hz, 1H), 5.63-5.58 (m, 1H), 4.89 (dd, *J* = 12.8, 6.5 Hz, 1H), 4.68 (dd, *J* = 12.8, 5.9 Hz, 1H), 3.80 (s, 3H), 2.03 (s, 3H). <sup>[7]</sup>

*N*-(2-nitro-1-p-tolylethyl)acetamide **2f** 



MeO

White solid; 99% ee;  $[\alpha]_D^{20} = -92.50$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C

at 8.0 °C/min;  $t_R = 26.3 \text{ min}$  (major),  $t_R = 27.5 \text{ min}$  (minor). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.20-7.15 (m, 4H), 6.16 (d, *J* = 6.1 Hz, 1H), 5.65-5.60 (m, 1H), 4.91 (dd, *J* = 12.8, 6.3 Hz, 1H), 4.71 (dd, *J* = 12.8, 5.8 Hz, 1H), 2.34 (s, 3H), 2.05 (s, 3H).<sup>[7]</sup>

N-(1-(4-trifluoromethylphenyl)-2-nitroethyl)acetamide 2g



White solid; 99.6% ee;  $[\alpha]_D{}^{20} = -46.30$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 29.5 min (major), t<sub>R</sub> = 36.9 min

(minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.64 (dd, *J* = 8.2 Hz, 1H), 7.44 (dd, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.76-5.71 (m, 1H), 4.91 (dd, *J* = 13.3, 6.5 Hz, 1H), 4.75 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.07 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.9,

140.4, 130.0 (q, J = 32.8 Hz), 126.9, 126.2 (q, 3.6 Hz), 123.7 (q, J = 273.5 Hz), 77.9, 50.8, 23.1. MALDI-HRMS Calculated for  $C_{11}H_{12}F_3N_2O_3^+$  ([M+H]<sup>+</sup>): 277.0795, found 277.0792.

N-(1-(3-fluorophenyl)-2-nitroethyl)acetamide 2h

White solid; 99% ee;  $[\alpha]_D^{20} = -55.80$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 26.1 min (major), t<sub>R</sub> = 29.4 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.32$ -7.27 (m, 1H), 7.03-6.94 (m, 3H), 6.24 (d, J = 5.76 Hz, 1H), 5.63-5.58 (m, 1H), 4.86-4.81 (dd, J = 13.2, 6.2 Hz, 1H), 4.69-4.64 (dd, J = 13.2, 5.2 Hz, 1H), 2.01 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 169.2$ , 162.1 (d, J = 246.2Hz), 138.1 (d, J = 6.6 Hz), 129.9(d, J = 8.2 Hz), 121.2 (d, J = 2.8 Hz), 114.7 (d, J =20.7 Hz), 112.7 (d, J = 22.5 Hz), 77.1, 49.9, 22.0. MALDI-HRMS Calculated for C<sub>10</sub>H<sub>11</sub>FKN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>):265.0385, found 265.0387.

N-(1-(4-chlorophenyl)-2-nitroethyl)acetamide 2i

White solid; 99.2% ee;  $[\alpha]_D{}^{20} = -66.70$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 8.0 mL/min, programmed from 110 °C to 190 °C at 15.0 °C/min; t<sub>R</sub> = 24.2 min (major), t<sub>R</sub> = 30.4 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.26-7.25 (m, 3H), 7.15-7.11 (m, 1H), 6.25 (d, *J* = 6.5 Hz, 1H), 5.61-5.56 (m, 1H), 4.85-4.81 (dd, *J* = 13.2, 6.3 Hz, 1H), 4.68-4.63 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.01 (s, 3H). <sup>[7]</sup>

N-(2-nitro-1-m-tolylethyl)acetamide 2j



White solid; 99% ee;  $[\alpha]_D^{20} = -71.20$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 24.1 min (major), t<sub>R</sub> = 25.0 min (minor). <sup>1</sup>H NMR

 $(400 \text{ MHz}, \text{CDCl}_3) \delta = 7.26-7.22 \text{ (m, 1H)}, 7.13-7.05 \text{ (m, 3H)}, 6.15 \text{ (d, } J = 7.0\text{Hz}, 1\text{H)}$ 5.60 (m, 1H), 4.88 (dd, J = 12.9, 6.3 Hz, 1H), 4.69 (dd, J = 12.9, 5.7 Hz, 1H), 2.32 (s,

#### 3H), 2.03 (s, 3H).<sup>[7]</sup>

N-(1-(3-methoxyphenyl)-2-nitroethyl)acetamide 2k

White solid; 99% ee;  $[\alpha]_D{}^{20} = -69.50$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 8.0 °C/min; t<sub>R</sub> = 39.2 min (major), t<sub>R</sub> = 41.2 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.32-7.28 (m, 1H), 6.89-6.83 (m, 3H), 6.22 (d, *J* = 7.3 Hz, 1H), 5.67-5.62 (m, 1H), 4.90 (dd, *J* = 13.0, 6.4 Hz, 1H), 4.72 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.81 (s, 3H), 2.06 (s, 3H).<sup>[7]</sup>

N-(1-(2-fluorophenyl)-2-nitroethyl)acetamide 21



White solid; 98% ee;  $[\alpha]_D{}^{20} = -69.80$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco beta Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 1.0 mL/min, programmed from 100 °C to 190 °C at 1.0 °C/min; t<sub>R</sub> = 83.5 min (minor), t<sub>R</sub> = 84.9 min (major). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.37-7.31 (m, 2H), 7.18-7.08 (m, 2H), 6.36 (d, *J* = 7.7 Hz, 1H), 5.92-5.86 (m, 1H), 4.90 (dd, *J* = 12.8, 6.7 Hz, 1H), 4.72 (dd, *J* = 12.8, 5.7 Hz, 1H), 2.06 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.8, 162.8 (d, *J* = 249.3Hz), 132.2 (d, *J* = 3.2Hz), 128.3 (d, *J* = 8.4Hz), 116.3 (d, *J* = 21.8Hz), 78.2, 50.7, 23.2. MALDI-HRMS Calculated for C<sub>10</sub>H<sub>11</sub>FKN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 265.0385, found 265.0388.

N-(1-(2-chlorophenyl)-2-nitroethyl)acetamide 2m



White solid; 99% ee;  $[\alpha]_D{}^{20} = -46.80$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco beta Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 1.0 mL/min, programmed from 100 °C to 190 °C at 1.0 °C/min; t<sub>R</sub> = 97.9 min (minor), t<sub>R</sub> = 99.4 min (major). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.38-7.36 (m, 1H), 7.31-7.23 (m, 3H), 6.58 (d, *J* = 7.2 Hz, 1H), 5.95 (m, 1H), 4.91 (dd, *J* = 13.0, 6.7 Hz, 1H), 4.75 (dd, *J* = 13.0, 5.0 Hz, 1H), 2.02 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.9, 159.8, 128.4, 127.8, 114.6, 78.2, 55.3, 51.0, 23.2. MALDI-HRMS Calculated for C<sub>10</sub>H<sub>11</sub>ClKN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 281.0090, found 281.0091.

*N*-(2-nitro-1-o-tolylethyl)acetamide 2n



White solid; 99.3% ee;  $[\alpha]_D{}^{20}$ = -92.30 (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco beta Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 0.8 mL/min, programmed from 100 °C to 190 °C at 0.8 °C/min; t<sub>R</sub> = 115.7 min (minor), t<sub>R</sub> = 118.9 min (major). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.54-7.50 (m, 4H), 6.25-6.19 (m, 2H), 5.15 (dd, *J* = 12.6, 6.68 Hz, 1H), 5.00 (dd, *J* = 12.6, 6.28 Hz, 1H), 2.74 (s, 3H), 2.32 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.8, 136.3, 134.7, 131.3, 128.8, 126.8, 125.0, 77.3, 47.9, 23.0, 19.2. MALDI-HRMS Calculated for C<sub>11</sub>H<sub>14</sub>KN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 261.0636, found 261.0642.

N-(1-(naphthalen-1-yl)-2-nitroethyl)acetamide 20



White solid; 97% ee;  $[\alpha]_D^{20} = -86.00$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); HPLC condition for corresponding acetamide: C-1 column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 230 nm; t<sub>R</sub> = 17.3 min (minor), t<sub>R</sub> = 35.6 min (major).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 8.09$  (d, J = 8.5 Hz, 1H), 7.91-7.85 (m, 2H),

7.64-7.53 (m, 2H), 7.47-7.42 (m, 2H) 6.55 (s, 1H), 6.19 (d, J = 7.6 Hz, 1H), 4.99 (dd, J = 12.8, 6.92 Hz, 1H), 4.79 (dd, J = 12.8, 6.2 Hz, 1H), 2.04 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.6, 134.1, 132.0, 130.4, 129.7, 129.2, 127.4, 126.4, 125.1, 123.2, 122.3, 47.5, 23.1. MALDI-HRMS Calculated for C<sub>14</sub>H<sub>14</sub>KN<sub>2</sub>O<sub>3</sub><sup>+</sup>([M+K]<sup>+</sup>): 297.0636, found 297.0642.

N-(1-(naphthalen-2-yl)-2-nitroethyl)acetamide 2p



White solid; 99% ee;  $[\alpha]_D^{20} = -116.00$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); HPLC condition for corresponding acetamide: C-1 column, hexane: isopropanol = 60:40; flow rate = 1.0 mL/min; UV detection at 230 nm; t<sub>R</sub> = 13.0 min (minor), t<sub>R</sub> = 23.7 min

(major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.87-7.80 (m, 3H), 7.76 (s, 1H), 7.53-7.49 (m, 2H), 7.39(dd, *J* = 8.5, 1.8 Hz, 1H) 6.43 (d, *J* = 7.5 Hz, 1H), 5.87-5.81 (m, 1H), 5.00 (dd, *J* = 13.0, 6.5 Hz, 1H), 4.81(dd, *J* = 13.0, 5.5 Hz, 1H), 2.08 (s, 3H).<sup>[7]</sup>

*N*-(1-furyl-2-nitroethyl)acetamide **2q** 



White solid; 97% ee;  $[\alpha]_D{}^{20} = -65.40$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 110 °C to 190 °C at 3.0 °C/min; t<sub>R</sub> = 25.8 min (major), t<sub>R</sub> = 26.8 min (minor). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.35 (s, 1H), 6.70 (d, *J* = 7.3 Hz, 1H), 6.32-6.29 (m, 1H), 5.77-5.73 (m, 1H), 4.85 (dd, *J* = 13.1, 5.9 Hz, 1H), 4.71 (dd, *J* = 13.1, 5.7 Hz, 1H), 2.01 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.9, 149.0, 142.9, 110.7, 108.0, 76.1, 45.5, 22.9. MALDI-HRMS Calculated for C<sub>8</sub>H<sub>10</sub>KN<sub>2</sub>O<sub>4</sub><sup>+</sup> ([M+K]<sup>+</sup>): 237.0272, found 237.0276.

N-(1-nitropentan-2-yl)acetamide 2r



White solid; 91% ee;  $[\alpha]_D{}^{20} = +43.6$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 100 °C to 190 °C at

5°C/min; t<sub>R</sub> = 16.9 min (major), t<sub>R</sub> = 17.9 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 5.80 (s, 1H), 4.56 (dd, J = 4.4, 1.4 Hz, 2H), 4.44-4.36 (m, 1H), 2.02 (s, 3H), 1.61-1.56 (m, 2H), 1.48-1.36 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 169.2, 77.1, 46.6, 32.5, 22.1, 18.2, 12.6. MALDI-HRMS Calculated for C<sub>7</sub>H<sub>14</sub>KN<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M+K]<sup>+</sup>): 213.0636, found 213.0642.

N-(3-methyl-1-nitrobutan-2-yl)acetamide 2s



ΗN

White solid; 96% ee;  $[\alpha]_D^{20} = +27.50$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco gamma Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 3.0 mL/min, programmed from 100 °C to 190 °C at 5°C/min; t<sub>R</sub> = 17.5 min (major), t<sub>R</sub> = 18.6 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  =

5.83 (d, J = 6.0 Hz, 1H), 4.63 (dd, J = 12.9, 5.7 Hz, 1H), 4.54 (dd, J = 12.9, 3.9 Hz, 1H), 4.24-4.17 (m, 1H), 2.04 (s, 3H), 1.94-1.85 (m, 1H), 1.03-0.98 (m, 6H).<sup>[7]</sup> *N*-(1-cyclohexyl-2-nitroethyl)acetamide 2t

White solid; 98% ee;  $[\alpha]_D^{20} = +26.20$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); GC condition: Supelco beta Dex<sup>TM</sup> 225 column (30 m × 0.25 mm × 0.25 µm), N<sub>2</sub> 1.0 mL/min, programmed from 100 °C to 190 °C at 1.0 °C/min; t<sub>R</sub> = 85.8 min (major), t<sub>R</sub> = 87.6 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.84 (d, *J* = 8.4 Hz, 1H), 4.66 (dd, *J* = 13.0, 5.5 Hz, 1H), 4.53 (dd, *J* = 13.0, 3.8 Hz, 1H), 4.26-4.19 (m,1H), 2.03 (s, 3H), 1.82-1.66 (m, 5H), 1.56-1.51 (m, 1H), 1.29-0.95 (m, 5H).<sup>[7]</sup>

## Reference

- [1] S.-F. Zhu, Y. Yang, L.-X. Wang, B. Liu, Q.-L. Zhou, Org. Lett. 2005, 7, 2333-2335.
- [2]W. Zhang, S.-F.Zhu, X.-C.Qiao, Q.-L.Zhou, Chem. Asian. J. 2008, 12, 2105-2111.
- [3]D. Xiao, X. Zhang, Angew. Chem. Int. Ed. 2001, 40, 3425-3428.
- [4] X.-F. Xia, X.-Z. Shu, K.-G. Ji, Y.-F. Yang, A. Shaukat, X.-Y. Liu, Y.-M. Liang, J. Org. Chem. 2010, 75, 2893-2896.
- [5] D. A. Heerding, T. J. Clark, D. H. Drewry, J. D. Leber, I. Safonov, D. S. Yamashita, WO011700A1, 2005.
- [6] S. Zhu, S. Yu, Y. Wang, D. Ma, Angew. Chem. Int. Ed. 2010, 49, 4656-4660.
- [7] M. Zhou, D. Dong, B. Zhu, H. Geng, Y. Wang, X. Zhang, Org. Lett. 2013, 15, 5524-5527.
- [8] B. M. Trost, C. Müller, J. Am. Chem. Soc. 2008, 130, 2438-2439.
- [9] X. Xu, T. Furukawa, T. Okino, H. Miyabe, Y. Takemoto, *Chem. Eur. J.* 2006, 12, 466-476.
- [10] A. J. Bloom, M. Fleischmann, J. M. Mellor, *Tetrahedron Lett.* 1984, 25, 4971-4974.

#### 8. NMR spectra of (R,R)-f-spiroPhos, 1, 2, and GC or HPLC spectra of 2

(*R*, *R*)-f-spiroPhos



(Z)-N-(2-nitro-1-phenylvinyl)acetamide 1a



(Z)-N-(1-(4-chlorophenyl)-2-nitrovinyl)acetamide 1c





(Z)-N-(1-(4-methoxyphenyl)-2-nitrovinyl)acetamide 1e



(Z)-N-(1-(4-trifluoromethylphenyl)-2-nitrovinyl)acetamide **1g** 









(Z/E)-N-(1-(2-fluorophenyl)-2-nitrovinyl)acetamide11



(Z)-N-(1-(2-chlorophenyl)-2-nitrovinyl)acetamide 1m







(Z)-N-(1-(naphthalen-1-yl)-2-nitrovinyl)acetamide 10



(Z)-N-(1-(naphthalen-2-yl)-2-nitrovinyl)acetamide 1p







(Z)-N-(3-methyl-1-nitrobut-1-en-2-yl)acetamide 1s





(Z)-N-(1-cyclohexyl-2-nitrovinyl)acetamide1t

*N*-(2-nitro-1-phenylethyl)acetamide 2a





N-(1-(4-fluorophenyl)-2-nitroethyl)acetamide 2b

*N*-(1-(4-chlorophenyl)-2-nitroethyl)acetamide **2c** 





*N*-(1-(4-methoxyphenyl)-2-nitroethyl)acetamide **2e** 



N-(2-nitro-1-p-tolylethyl)acetamide **2f** 



N-(1-(4-trifluoromethylphenyl)-2-nitroethyl)acetamide **2g** 







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*N*-(2-nitro-1-m-tolylethyl)acetamide **2j** 







*N*-(1-(2-chlorophenyl)-2-nitroethyl)acetamide **2m** 







*N*-(1-(naphthalen-1-yl)-2-nitroethyl)acetamide **20** 



*N*-(1-(naphthalen-2-yl)-2-nitroethyl)acetamide **2p** 

![](_page_43_Figure_0.jpeg)

N-(1-nitropentan-2-yl)acetamide 2r

![](_page_43_Figure_2.jpeg)

![](_page_44_Figure_0.jpeg)

N-(3-methyl-1-nitrobutan-2-yl)acetamide 2s

![](_page_44_Figure_2.jpeg)

N-(1-cyclohexyl-2-nitroethyl)acetamide 2t

![](_page_45_Figure_1.jpeg)

![](_page_46_Figure_0.jpeg)

![](_page_46_Figure_1.jpeg)

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[pA*s]	[pA]	00
1	21.912	BB	0.1938	963.61115	70.15589	99.40322
2	23.335	BB	0.1777	5.78518	4.25786e-1	0.59678
Total	s:			969.39632	70.58168	

![](_page_47_Figure_0.jpeg)

![](_page_47_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- ---- ---- ---- 

 1
 26.302
 BB
 0.8369
 1.06184e4
 160.28734
 99.37873

 2
 30.409
 BB
 0.6179
 66.38152
 1.71524
 0.62127

 Totals :
 1.06848e4
 162.00258

![](_page_48_Figure_0.jpeg)

![](_page_48_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- ---- ---- ---- 

 1
 28.008
 BB
 1.6716
 2.65044e4
 191.58089
 99.95192

 2
 35.866
 BB
 0.4369
 12.74998
 4.36324e-1
 0.04808

 Totals :
 2.65172e4
 192.01721

![](_page_49_Figure_0.jpeg)

![](_page_49_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- ---- ---- ---- 

 1
 41.655
 BB
 2.5679
 2.46950e4
 114.33097
 1.000e2

 Totals :
 2.46950e4
 114.33097

![](_page_50_Figure_0.jpeg)

![](_page_50_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- --- --- --- 

 1
 46.333
 BB
 0.5793
 7392.43896
 152.24339
 99.62868

 2
 49.379
 BB
 0.5599
 27.55218
 6.16356e-1
 0.37132

 Totals :
 7419.99114
 152.85975

![](_page_51_Figure_0.jpeg)

![](_page_51_Figure_1.jpeg)

Peak	Ret Ti me	Туре	Width	Area	Hei ght	Area
#	[min]		[min]	[pA*s]	[pA]	%
1	26.340	BV	0.5514	1.67046e4	523.67102	99. 39737
2	27.510	VB	0.3635	101.27671	4.52551	0. 60263
Total	s:			1.68059e4	528. 19653	

![](_page_52_Figure_0.jpeg)

![](_page_52_Figure_1.jpeg)

Peak RetTime Type Width Area Hei ght Area [pA\*s] # [min] [min] [pA] % 1 29.497 VV 1.6186 2.58043e4 187.66515 99.77208 2 36.914 VV 0. 5468 58. 94838 1.27270 0.22792 Totals : 2.58633e4 188.93784

![](_page_53_Figure_0.jpeg)

![](_page_53_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- ---- ---- ---- 

 1
 26.135
 BB
 0.4272
 1811.25854
 60.30832
 99.36621

 2
 29.378
 BB
 0.3109
 11.55287
 6.09188e-1
 0.63379

 Totals :
 1822.81141
 60.91751

![](_page_54_Figure_0.jpeg)

![](_page_54_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- --- --- --- 

 1
 24.230
 BB
 1.0453
 3.02557e4
 359.69955
 99.60504

 2
 30.385
 BB
 1.0479
 119.97150
 1.66013
 0.39496

 Totals :
 3.03757e4
 361.35969

![](_page_55_Figure_0.jpeg)

![](_page_55_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- --- --- --- 

 1
 24.086
 VV
 0.2977
 9117.00586
 407.66019
 99.41799

 2
 25.027
 VB
 0.2526
 53.37218
 3.21991
 0.58201

 Totals :
 9170.37804
 410.88010

![](_page_56_Figure_0.jpeg)

![](_page_56_Figure_1.jpeg)

Peak RetTime Type Width Height Area Area % # [min] [min] [pA\*s] [pA] ---- | - - - - - - | - - - - | ------ - - - - - - - - -- - - - - - - - -1 39.176 BB 0. 4279 4260. 60596 119. 75010 99. 33835 2 41.206 BB 0.3770 28.37811 9.05123e-1 0.66165 Totals : 4288.98407 120.65522

![](_page_57_Figure_0.jpeg)

![](_page_57_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA]
 %

 --- --- --- ---- ---- 

 1
 83.471
 BB
 0.1618
 88.24049
 8.23541
 1.21183

 2
 84.879
 BB
 0.3282
 7193.32715
 266.05344
 98.78817

 Totals :
 7281.56763
 274.28885

![](_page_58_Figure_0.jpeg)

![](_page_58_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 ----|-----|
-----
 -----|
 1.60012
 0.75412

 2
 99.449
 VB
 0.4978
 3761.79272
 90.93818
 99.24588

 Totals :
 3790.37679
 92.53830

![](_page_59_Figure_0.jpeg)

![](_page_59_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- --- --- --- 

 1
 115.715
 BV
 0.3197
 70.57587
 2.99528
 0.35729

 2
 118.870
 VB
 1.0554
 1.96825e4
 221.27208
 99.64271

 Totals :
 1.97531e4
 224.26735

![](_page_60_Figure_0.jpeg)

![](_page_60_Figure_1.jpeg)

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
 1 2	17.264 35.573	 BB BB	0.8261 1.5547	222.36137 1.47931e4	4.07176 143.14575	 1.4809 98.5191
Total	ls :			1.50155e4	147.21751	

![](_page_61_Figure_0.jpeg)

![](_page_61_Figure_1.jpeg)

Peak #	RetTime [min]	туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.041	VB	0.5174	493.91513	14.57329	0.7417
2	23.678	VB	1.0529	6.61017e4	990.08136	99.2583
Total	ls :			6.65956e4	1004.65465	

![](_page_62_Figure_0.jpeg)

![](_page_62_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 ----|-----|
-----
 -----|

 1
 25.805
 BB
 0.1714
 3296.75977
 227.05684
 98.31242

 2
 26.816
 BB
 0.0767
 56.59031
 8.74770
 1.68758

 Totals :
 3353.35007
 235.80454

![](_page_63_Figure_0.jpeg)

![](_page_63_Figure_1.jpeg)

Peak #	RetTime [min]	Туре	Width [min]	Area [pA*s]	Height [pA]	Area %
1	16.897	BB	0.1792	6538.93359	428.66077	95.28071
2	17.861	BB	0.0599	323.87592	64.32095	4.71929
Total	ls :			6862.80951	492.98171	

![](_page_64_Figure_0.jpeg)

![](_page_64_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- --- --- %

 1
 17.465
 BB
 0.1561
 3582.47803
 285.32629
 98.04352

 2
 18.585
 BB
 0.0608
 71.48896
 18.59858
 1.95648

 Totals :
 3653.96699
 303.92487

![](_page_65_Figure_0.jpeg)

![](_page_65_Figure_1.jpeg)

 Peak RetTime Type
 Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 --- --- --- --- --- --- 

 1
 85.823
 BB
 0.4469
 6719.51123
 188.21558
 98.92183

 2
 87.641
 BB
 0.3139
 73.23739
 2.79312
 1.07817

 Totals :
 6792.74862
 191.00870