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Synthesis of Enantiomerically Enriched Imidazolidin-2-Ones through Asymmetric Palladium-Catalyzed Alkene Carboamination Reactions**

Brett A. Hopkins and John P. Wolfe*

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Brett A. Hopkins and John P. Wolfe*

Department of Chemistry, University of Michigan, 930 N. University Avenue, Ann Arbor, Michigan 48109-1055

Supporting Information

Experimental procedures and characterization data for new compounds.

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General: Reactions were carried out under nitrogen in flame-dried glassware. Tris(dibenzylideneacetone)dipalladium and (S)-Siphos-PE were purchased from Strem Chemical Co. and used without further purification. All other reagents including all aryl and alkenyl bromides were purchased from commercial sources and used as received unless otherwise noted. Xylenes were purified by distillation over CaH₂ prior to use in
reactions. Methylene chloride and toluene were purified using a GlassContour solvent system. All yields refer to isolated compounds that are estimated to be $\geq$95% pure as judged by $^1$H NMR analysis. The yields reported in the supporting information describe the result of a single experiment, whereas yields reported in Tables 1–2 and equations 2–4 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Table 2 and equations 2–4.

**General procedure for the synthesis of N-allylurea substrates.** A flame-dried round bottom flask equipped with a stirbar was cooled under a stream of nitrogen. The flask was charged with the appropriate isocyanate (1.0 equiv) and methylene chloride (0.60 M). The resulting solution was cooled to 0 °C and stirred for 5 min, then the allylic amine (1.1 equiv) was added dropwise. The solution was warmed to rt and stirred for five h. The mixture was then concentrated in vacuo and purified by flash chromatography on silica gel.

![Structural formula](image)

**1-Allyl-3-{4-[benzyl(methyl)amino]phenyl}-1-methylurea (1a):** A flame dried Schlenk flask equipped with a stirbar was cooled under a stream of nitrogen and charged with 1-allyl-3-(4-bromophenyl)-1-methylurea (1.00 g, 3.72 mmol), lithium bis(trimethylsilyl)amide (1.37 g, 4.46 mmol), Pd$_2$(dba)$_3$ (34.1 mg, 0.0372 mmol), and DavePhos (35.1 mg, 0.0893 mmol). The flask was purged with N$_2$ pressure for 30 s then THF (8.2 mL) and N-methyl benzylamine (0.58 mL, 4.46 mmol) were added. The
resulting mixture was heated to 65 °C with stirring for 15 h, then was cooled to rt. A solution of 1M HCl (8 mL) was added and the resulting mixture was stirred at rt for five min. A solution of saturated aqueous NaHCO₃ (8 mL) was slowly added and the mixture was transferred to a separatory funnel after bubbling ceased. The mixture was extracted with ethyl acetate (3 x 20 mL) then the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to afford 450 mg (40%) of the title compound as a light brown solid, mp 93–97 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.14 (m, 7H), 6.68 (d, J = 9.0 Hz, 2H), 6.18 (s, br, 1H), 5.83 (ddt, J = 5.5, 5.2, 12.0 Hz, 1H), 5.26–5.19 (m, 2H), 4.46 (s, 2H), 3.93 (d, J = 5.5 Hz, 2H), 2.96 (s, 3H), 2.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 146.5, 138.9, 133.6, 128.4, 128.8, 126.8, 126.7, 122.5, 116.7, 113.0, 57.0, 51.4, 38.7, 34.4; IR (film) 1637 cm⁻¹. MS (Cl) 310.1916 (310.1914 calcd for C₁₉H₂₃N₃O, M + H⁺).

1-Allyl-3-(4-methoxyphenyl)-1-methylurea (1b): The reaction of N-allylmethylamine (0.47 mL, 4.92 mmol) with 4-methoxyphenyl isocyanate (0.58 mL, 4.47 mmol) according to the general procedure afforded 841 mg (85%) of the title compound as a white solid, mp 52–55 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 6.61 (s, br, 1H), 5.90–5.78 (m, 1H), 5.25 (d, J = 5.5 Hz, 1H), 5.22 (s, 1H), 3.94 (d, J = 5.3 Hz, 2H), 3.76 (s, 3H), 2.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 155.7,
133.5, 132.2, 122.1, 116.8, 114.0, 55.5, 51.5, 34.5; IR (film) 1638 cm$^{-1}$. MS (Cl) 221.1280 (221.1285 calcd for C$_{12}$H$_{16}$N$_2$O$_2$, M + H$^+$).

1-Allyl-1-methyl-3-phenylurea (1c): The reaction of N-allylmethylamine (0.37 mL, 3.85 mmol) with phenyl isocyanate (0.42 mL, 3.50 mmol) according to the general procedure afforded 644 mg (88%) of the title compound as a white solid, mp 71–74 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.48 (s, br, 1H), 5.88–5.78 (m, 1H), 5.26–5.19 (m, 2H), 3.93 (d, J = 5.5 Hz, 2H), 2.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.6, 139.2, 133.4, 128.8, 122.9, 119.8, 116.9, 51.5, 34.5; IR (film) 1639 cm$^{-1}$. MS (Cl) 191.1180 (191.1179 calcd for C$_{11}$H$_{14}$N$_2$O, M + H$^+$).

1-Allyl-3-(4-bromophenyl)-1-methylurea (1d): The reaction of N-allylmethylamine (0.80 mL, 8.44 mmol) with 4-bromophenyl isocyanate (1.51 g, 7.67 mmol) according to the general procedure afforded 1.88 g (91%) of the title compound as a white solid, mp 123–126 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.9 Hz,
2H), 6.47 (s, br, 1H), 5.81 (ddt, J = 5.5, 5.6, 9.9 Hz, 1H), 5.27–5.19 (m, 2H), 3.92 (d, J = 5.3 Hz, 2H), 2.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 138.3, 133.2, 131.7, 121.4, 117.0, 115.2, 51.5, 34.6; IR (film) 1634 cm$^{-1}$. MS (Cl) 269.0282 (269.0284 calcd for C$_{11}$H$_{13}$BrN$_2$O, M + H$^+$).

1-Allyl-3-(4-cyanophenyl)-1-methylurea (1e): The reaction of N-allylmethylamine (0.73 mL, 7.65 mmol) with 4-cyanophenyl isocyanate (1.00 g, 6.96 mmol) according to the general procedure afforded 1.17 g (78%) of the title compound as a white solid, mp 119–122 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 6.69 (s, br, 1H), 5.86 (ddt, J = 5.1, 5.4, 11.9 Hz, 1H), 5.32–5.25 (m, 2H), 3.80 (d, J = 5.4 Hz, 2H), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.6, 143.5, 133.1, 132.9, 119.2, 119.0, 117.4, 105.3, 51.6, 34.8; IR (film) 1664 cm$^{-1}$. MS (Cl) 216.1135 (216.1131 calcd for C$_{12}$H$_{13}$N$_3$O$_3$, M + H$^+$).

1-Allyl-1-methyl-3-(4-nitrophenyl)urea (1f): The reaction of N-allylmethylamine (0.77 mL, 8.09 mmol) with 4-nitrophenyl isocyanate (1.21 g, 7.35 mmol) according to the general procedure afforded 1.61 g (93%) of the title compound as a yellow solid, mp
78–81 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, $J = 9.2$ Hz, 2H), 7.53 (d, $J = 9.2$ Hz, 2H), 7.00 (s, br, 1H), 5.84 (ddt, $J = 5.3$, 5.6, 11.4 Hz, 1H), 5.32–5.22 (m, 2H), 3.98 (d, $J = 5.3$ Hz, 2H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.7, 145.6, 142.2, 132.8, 125.0, 118.4, 117.4, 51.6, 34.8; IR (film) 1660 cm$^{-1}$. MS (Cl) 236.1037 (236.1030 calcd for C$_{11}$H$_{13}$N$_3$O$_3$, M + H$^+$).

1-Methyl-1-(2-methylallyl)-3-(4-nitrophenyl)urea (3): A flame dried flask equipped with a stirbar was cooled under a stream of nitrogen and charged with 3-bromo-2-methylpropene (4.60 mL, 45 mmol). The flask was cooled to 0 °C and stirred for five min, then methylamine (27.2 mL, 225 mmol, 33% solution in EtOH) was added and the resulting mixture was warmed to rt and stirred for 15 h. A solution of 1M NaOH (20 mL) was added and the resulting mixture was transferred to a separatory funnel. The mixture was extracted with ether (3 x 20 mL) then the combined organic layers were washed with 1M NaOH (1x12 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and partially concentrated in vacuo (to remove excess methylamine) to afford N,N-dimethylprop-2-en-1-ylamine as a solution in ethanol. The solution was transferred to a flask equipped with a stirbar and cooled to −10 °C. Neat 4-nitrophenyl isocyanate (1.64 g, 10 mmol) was added and the resulting solution and the reaction was slowly warmed to rt over the course of five h. The reaction mixture was then concentrated in vacuo and the crude
product was purified by flash column chromatography to yield 350 mg (14%) of the title compound as a yellow solid, mp 79–82 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, J = 9.3 Hz, 2H), 7.52 (d, J = 9.1 Hz, 2H), 6.92 (s, br, 1H), 6.03 (s, 1H) 4.96 (s, 1H), 3.90 (s, 2H), 3.05 (s, 3H), 1.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.7, 145.5, 142.3, 141.0, 125.0, 118.3, 112.5, 55.2, 35.3, 19.7; IR (film) 1658 cm⁻¹. MS (Cl) 250.1191 (250.1186 calcd for C₁₂H₁₅N₃O₃, M + H⁺).

1-Cinnamyl-1-methyl-3-(4-nitrophenyl)urea (5): A flame dried flask equipped with a stirbar was cooled under a stream of nitrogen and charged with cinnamyl bromide (4.33 g, 22 mmol). The flask was cooled to 0 °C and stirred for five min, then methylamine (27.2 mL, 225 mmol, 33% solution in EtOH) was added and the resulting mixture was warmed to rt and stirred for 15 h. A solution of 1M NaOH (20 mL) was added and the resulting mixture was transferred to a separatory funnel. The mixture was extracted with ether (3 x 20 mL) then the combined organic layers were washed with 1M NaOH (1x12 mL), dried over anhydrous Na₂SO₄, filtered, and partially concentrated in vacuo (to remove excess methylamine) to afford (E)-N-methyl-3-phenylprop-2-en-1-ylamine as a solution in ethanol. The solution was transferred to a flask equipped with a stirbar and cooled to −10 °C. Neat 4-nitrophenyl isocyanate (1.44g, 8.8 mmol) was added and the resulting solution and the reaction was slowly warmed to rt over the course of five h. The reaction mixture was then concentrated in vacuo and the crude product was purified by flash column chromatography to yield 430 mg (16%) of the title compound as
a white solid, mp 120–124 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.14 (d, $J = 9.1$ Hz, 2H), 7.55 (d, $J = 9.3$ Hz, 2H), 7.40 (d, $J = 7.3$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.28 (t, $J = 7.1$ Hz, 1H), 6.92 (s, br, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 6.23 (dt, $J = 5.9, 15.9$ Hz, 1H), 4.17 (d, $J = 5.9$ Hz, 2H), 3.10 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.5, 145.4, 142.4, 135.9, 132.8, 128.7, 128.2, 126.5, 125.1, 123.9, 118.4, 51.2, 34.8; IR (film) 1659 cm$^{-1}$. MS (Cl) 312.1353 (312.1343 calcd for C$_{17}$H$_{17}$N$_3$O$_3$, M + H$^+$).

**General procedure for asymmetric Pd-catalyzed carboamination reactions of N-allylurea derivatives.** A flame-dried Schlenk tube equipped with a stirbar was cooled under a stream of nitrogen and then charged with Pd$_2$(dba)$_3$ (2 mol %), (S)-Siphos-PE (6 mol %), the urea substrate (1.0 equiv), and NaO'Bu (2.0 equiv). The flask was purged with N$_2$, then the aryl or alkenyl halide (2.0 equiv), the additive (H$_2$O, 2.0 equiv; or TFA, 40 mol % if needed) and xylenes (0.20 M, for reactions at 120 °C) or toluene (0.20 M, for reactions at 90 °C) were added. The resulting mixture was heated to 90 °C or 120 °C with stirring until the starting material had been consumed as judged by TLC analysis. The reaction mixture was then cooled to rt, saturated aqueous ammonium chloride (6mL/mmol substrate) was added, and the mixture was transferred to a separatory funnel. The mixture was extracted with ethyl acetate (3 x 5 mL) then the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.
(−)-(4S)-3-{4-[Benzyl(methyl)amino]phenyl}-4-[4-(tert-butyl)benzyl]-1-

methylimidazolidin-2-one (2a). The general procedure was employed for the coupling
of 1-allyl-3-{4-[benzyl(methyl)amino]phenyl}-1-methylurea (0.10 mmol, 30.9 mg) and 4-
bromo-tert-butylbenzene (0.20 mmol, 42.6 mg), using a catalyst composed of Pd₂dba₃-
(0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature
of 90 °C, and a reaction time of 12 h. This procedure afforded the title compound (28.7
mg, 65%) as an orange oil: [α]23D −23.2 (c 0.68, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ
7.34–7.23 (m, 9H), 7.05 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 4.52 (s, 2H), 4.28–
4.20 (m, 1H), 3.30 (app. t, J = 8.6 Hz, 1H), 3.12 (dd, J = 6.1, 8.8 Hz, 1H), 3.06 (dd, J =
3.3, 13.7 Hz, 1H), 3.00 (s, 3H), 2.79 (s, 3H) 2.58 (dd, J = 10.0, 13.5 Hz, 1H), 1.30 (s,
9H); ¹³C NMR (125 MHz, CDCl₃); 159.5, 149.6, 147.3, 139.0, 133.8, 128.8, 128.6,
128.2, 126.9, 126.8, 125.5, 124.5, 112.9, 57.0, 55.9, 50.1, 38.7, 38.0, 34.4, 31.4, 31.3;
IR (film) 1704 cm⁻¹; MS (CI) 442.2866 (442.2859 calcd for C₂₉H₃₅N₃O, M + H⁺). The
enantiopurity was determined to be 73% ee by chiral HPLC analysis (chiralcel ADH, 25
cm x 4.6 mm, 15% IPA/Hexanes, 1.50 mL/min, λ 198 nm, RT= 6.1 and 9.2 min).
(−)(4S)-4-[4-(tert-Butyl)benzyl]-3-(4-methoxyphenyl)-1-methylimidazolidin-2-one (2b). The general procedure was employed for the coupling of 1-allyl-3-(4-methoxyphenyl)-1-methylurea (0.10 mmol, 22.1 mg) and 4-bromo-tert-butylbenzene (0.20 mmol, 42.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 90 °C, and a reaction time of 12 h. This procedure afforded the title compound (33.0 mg, 93%) as an orange oil: $[\alpha]_{D}^{23} -10.1 \ (c \ 0.76, \text{CH}_2\text{Cl}_2)$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 9.0$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 7.06 (d, $J = 8.3$ Hz, 2H), 6.93 (d, $J = 9.0$ Hz, 2H), 4.37–4.29 (m, 1H), 3.82 (s, 3H), 3.36 (app. t, $J = 8.7$ Hz, 1H), 3.17 (dd, $J = 5.9$, 9.2 Hz, 1H), 3.05 (dd, $J = 3.7$, 13.7 Hz, 1H), 2.81 (s, 3H), 2.62 (dd, $J = 9.8$, 13.7 Hz, 1H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) 159.0, 156.4, 149.6, 133.5, 131.8, 128.8, 125.5, 123.8, 114.3, 55.5, 55.4, 49.8, 37.8, 34.4, 31.3, 31.2; IR (film) 1700 cm$^{-1}$; MS (CI) 353.2232 (353.2224 calcd for C$_{22}$H$_{28}$N$_2$O$_2$, M + H$^+$). The enantiopurity was determined to be 79% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.50 mL/min, λ 198 nm, RT= 5.3 and 8.1 min).
(−)-(4S)-4-[4-(tert-Butyl)benzyl]-1-methyl-3-phenylimidazolidin-2-one (2c). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-phenylurea (0.10 mmol, 17.6 mg) and 4-bromo-tert-butylbenzene (0.20 mmol, 42.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 90 °C and a reaction time of 12 h. This procedure afforded the title compound (29.0 mg, 90%) as white solid, mp 67–70 °C: [α$^{23}_D$] $-19.4$ (c 0.55, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J = 8.6$ Hz, 2H), 7.37 (t, $J = 7.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.12–7.06 (m, 3H), 4.48–4.40 (m, 1H), 3.37 (app. t, $J = 8.6$ Hz, 1H), 3.20 (dd, $J = 4.9$, 8.4 Hz, 1H), 3.11 (dd, $J = 3.3$, 13.8 Hz, 1H), 2.81 (s, 3H), 2.64 (dd, $J = 9.8$, 13.8 Hz, 1H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) 158.3, 149.7, 138.9, 133.5, 129.0, 128.8, 125.6, 123.4, 120.7, 54.4, 49.4, 37.5, 34.4, 31.3, 31.0; IR (film) 1707 cm$^{-1}$; MS (Cl) 323.2125 (323.2118 calcd for C$_{21}$H$_{26}$N$_2$O, M + H$^+$). The enantiopurity was determined to be 78% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 8% IPA/Hexanes, 1.0 mL/min, λ 198 nm, RT= 9.5 and 10.1 min).
(-)-(4S)-3-(4-Bromophenyl)-4-[4-(tert-butyl)benzyl]-1-methylimidazolidin-2-one (2d). The general procedure was employed for the coupling of 1-allyl-3-(4-bromophenyl)-1-methylurea (0.10 mmol, 26.9 mg) and 4-bromo-tert-butylbenzene (0.20 mmol, 42.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 90 °C and a reaction time of 12 h. This procedure afforded the title compound (18.0 mg, 45%) as an orange oil: [α]$^\text{D}$$^23$ = -41.6 (c 0.42, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.49–7.43 (m, 4H), 7.32 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 4.44–4.38 (m, 1H), 3.39 (app. t, J = 8.8 Hz, 1H), 3.22 (dd, J = 4.6, 9.0 Hz, 1H), 3.07 (dd, J = 3.7, 13.8 Hz, 1H), 2.82 (s, 3H), 2.66 (dd, J = 9.5, 13.8 Hz, 1H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) 157.9, 150.0, 138.1, 133.3, 131.9, 128.8, 125.6, 121.9, 116.0, 54.2, 49.2, 37.4, 34.3, 31.3, 31.9; IR (film) 1708 cm$^{-1}$; MS (Cl) 401.1230 (401.1223 calcd for C$_{21}$H$_{25}$BrN$_2$O, M + H$^+$). The enantiopurity was determined to be 83% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.50 mL/min, λ 198 nm, RT= 4.3 and 6.0 min).
(-)-(5S)-4-{5-[4-(tert-Butyl)benzyl]-3-methyl-2-oxoimidazolidin-1-yl}benzonitrile

(2e): The general procedure was employed for the coupling of 1-allyl-3-(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 4-bromo-tert-butylbenzene (0.20 mmol, 42.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound (30.2 mg, 87%) as a light orange solid, mp 108–113 °C: [α]$^D$_23.6 = –73.6 (c 0.91, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J$ = 9.0 Hz, 2H), 7.63 (d, $J$ = 9.0 Hz, 2H), 7.35 (d, $J$ = 8.3 Hz, 2H), 7.10 (d, $J$ = 8.3 Hz, 2H), 4.50 (m, 1H), 3.46 (app. t, $J$ = 8.8 Hz, 1H), 3.28 (dd, $J$ = 3.5, 9.2 Hz, 1H), 3.10 (dd, $J$ = 3.5, 14.1 Hz, 1H), 2.83 (s, 3H) 2.73 (dd, $J$ = 9.2, 14.0 Hz, 1H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.9, 150.2, 143.2, 133.1, 132.6, 128.8, 125.7, 119.2, 118.5, 105.0, 53.6, 48.7, 37.3, 34.5, 31.3, 30.8; IR (film) 1712 cm$^{-1}$; MS (Cl) 348.2082 (348.2070 calcd for C$_{22}$H$_{25}$N$_3$O, M + H$^+$). The enantiopurity was determined to be 86% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 198 nm, RT= 5.4 and 8.6 min).
(−)-(4S)-4-[4-(tert-Butyl)benzyl]-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one  (2f).

The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-bromo-tert-butylbenzene (0.40 mmol, 85.2 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (59.6 mg, 81%) and 91% ee as a bright yellow solid, mp 115–118 °C: [α]$^{23}_D$ –102.3 (c 1.49, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.22 (d, $J$ = 9.2 Hz, 2H), 7.78 (d, $J$ = 9.4 Hz, 2H), 7.34 (d, $J$ = 8.2 Hz, 2H), 7.9 (d, $J$ = 8.2 Hz, 2H), 4.56–4.49 (m, 1H), 3.48 (app. t, $J$ = 9.0 Hz, 1H), 3.29 (dd, $J$ = 3.0, 9.3 Hz, 1H), 3.11 (dd, $J$ = 3.5, 13.8 Hz, 1H), 2.83 (s, 3H), 2.75 (dd, $J$ = 9.0, 13.9 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 150.3, 145.2, 141.9, 132.5, 128.8, 125.8, 125.0, 117.7, 53.7, 48.6, 37.3, 34.5, 31.3, 30.8; IR (film) 1717 cm$^{-1}$. MS (Cl) 368.1968 (368.1969 calcd for C$_{21}$H$_{25}$N$_3$O$_3$, M + H$^+$). The enantiopurity was determined to be 92% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.50 mL/min, λ 198 nm, RT= 6.1 and 9.4 min).

(−)-(4S)-4-[4-(tert-Butyl)benzyl]-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one  (X).

The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.10 mmol, 23.5 mg) and 4-iodo-tert-butylbenzene (0.20 mmol, 52.0
mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (19.0 mg, 60%) as a bright yellow solid. This material contained ca 35% of an inseparable unidentified regioisomer. The enantiopurity was determined to be 47% ee by chiral HPLC analysis. Spectroscopic data were identical to those reported above.

(−)-(4S)-1-Methyl-3-(4-nitrophenyl)-4-[4-(trifluoromethyl)benzyl]imidazolidin-2-one (2g). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-bromobenzotri fluoride (0.40 mmol, 90.0 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), H$_2$O (0.40 mmol, 7 μL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (54.6 mg, 72%) as a bright yellow solid, mp 161–164 °C: [α]$^D_{23} = -75.1$ (c 11.5, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, $J = 9.2$ Hz, 2H), 7.78 (d, $J = 9.3$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 4.64–4.58 (m, 1H), 3.51 (app. t, $J = 9.0$ Hz, 1H), 3.24 (dd, $J = 3.1, 9.3$ Hz, 1H), 3.17 (dd, $J = 3.1, 9.3$ Hz, 1H), 3.01 (dd, $J = 8.6, 14.0$ Hz, 1H), 2.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.5, 144.8, 142.1, 139.6, 129.6 (q,
65.2 Hz), 129.5, 125.8 (q, 3.81), 125.1, 123.9 (q, 272.0 Hz), 117.8, 53.2, 48.3, 37.5, 30.7; IR (film) 1708 cm\(^{-1}\). MS (Cl) 380.1211 (380.1217 calcd for C\(_{18}\)H\(_{16}\)F\(_3\)N\(_3\)O\(_3\), M + H\(^+\)). The enantiopurity was determined to be 95% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, \(\lambda\) 195 nm, RT= 9.3 and 16.8 min).

\(-\)-(4S)-1-Methyl-3-(4-nitrophenyl)-4-[3-(trifluoromethyl)benzyl]imidazolidin-2-one (2h). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 3-bromobenzotrifluoride (0.40 mmol, 90.0 mg) using a catalyst composed of Pd\(_2\)(dba)\(_3\) (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), H\(_2\)O (0.40 mmol, 7 \(\mu\)L) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (53.1 mg, 70%) as a bright yellow solid, mp 145–148 °C: \([\alpha]^{23}_{D}\) –64.1 (c 1.16, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.22 (d, \(J = 9.0\) Hz, 2H), 7.77 (d, \(J = 9.0\) Hz, 2H), 7.53 (d, \(J = 7.8\) Hz, 1H), 7.44 (t, \(J = 7.6\) Hz, 1H), 7.38 (s, 1H), 7.32 (d, \(J = 7.6\) Hz, 1H), 4.65–4.58 (m, 1H), 3.53 (app. t, \(J = 9.0\) Hz, 1H), 3.24 (dd, \(J = 2.7, 9.2\) Hz, 1H), 3.15 (dd, \(J = 3.5, 14.1\) Hz, 1H), 2.93 (dd, \(J = 8.4, 14.0\) Hz, 1H), 2.79 (s, 3H); \(^1^\)3C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 156.5, 144.9, 142.1, 136.1, 132.7, 131.2 (q, \(J = 32.4\) Hz), 129.4, 125.8 (q, \(J = 3.8\) Hz), 125.1, 124.2 (q, \(J = 3.8\) Hz), 123.9 (q, \(J = 271.8\) Hz), 117.8, 53.1, 48.4, 37.6, 30.7; IR
(–)-(4S)-1-Methyl-3-(4-nitrophenyl)-4-[2-(trifluoromethyl)benzyl]imidazolidin-2-one (2i). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 2-bromobenzotrifluoride (0.40 mmol, 90.0 mg), using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), H$_2$O (0.40 mmol, 7 µL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (42.5 mg, 56%) as a bright yellow solid, mp 70–73 °C: [α]$^2$$^3_D$ –98.7 (c 0.72, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, J = 9.0 Hz, 2H), 7.72–7.64 (m, 3H), 7.44 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 4.72–4.64 (m, 1H), 3.43 (app. t, J = 9.0 Hz, 1H), 3.36 (dd, J = 5.1, 14.4 Hz, 1H), 3.20 (dd, J = 2.0, 9.3 Hz, 1H), 2.96 (dd, J = 9.0, 14.3 Hz, 1H), 2.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 145.1, 142.0, 134.4, 132.1, 129.2 (q, J = 30.0 Hz), 127.5, 126.6 (q, J = 5.7 Hz), 124.8, 124.4 (q, J = 272.3 Hz), 118.0, 53.1, 48.3, 35.0, 30.9 (one peak is missing due to incidental equivalence); IR (film) 1722 cm$^{-1}$. MS (Cl) 380.1226 (380.1217 calcd for C$_{18}$H$_{16}$F$_3$N$_3$O$_3$, M + H$^+$. The
enantiopurity was determined to be 83% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 195 nm, RT = 7.9 and 12.5 min).

\((-\))-(4S)-4-(4-Benzoylbenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (2j). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-bromobenzophenone (0.40 mmol, 104.4 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), H$_2$O (0.40 mmol, 7 µL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (68.1 mg, 82%) as a bright yellow solid, mp 115–118 °C: [α]$^23_D$ = -53.7 (c 0.97, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, $J$ = 9.3 Hz, 2H), 7.80–7.72 (m, 6H), 7.57 (t, $J$ = 7.4 Hz, 1H), 7.46 (t, $J$ = 7.8 Hz, 2H), 7.26 (d, $J$ = 8.2 Hz, 2H), 4.65–4.58 (m, 1H), 3.50 (app. t, $J$ = 9.0 Hz, 1H), 3.26 (dd, $J$ = 3.1, 9.2 Hz, 1H), 3.18 (dd, $J$ = 3.5, 14.0 Hz, 1H), 2.91 (dd, $J$ = 8.8, 13.9 Hz, 1H), 2.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.1, 156.6, 145.0, 142.1, 140.3, 137.3, 136.6, 132.6, 130.6, 130.0, 129.2, 128.4, 125.1, 117.8, 53.2, 48.4, 37.8, 34.4, 30.8; IR (film) 1715, 1657 cm$^{-1}$. MS (CI) 416.1620 (416.1605 calcd for C$_{24}$H$_{21}$N$_3$O$_4$, M + H$^+$). The enantiopurity was determined to be 86% ee by chiral HPLC.
analysis (ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 195 nm, RT= 39.0 and 54.9 min.)

\[(-)-(4S)-4-(4-Fluorobenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one \text{ (2k).}\] The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-bromofluorobenzene (0.40 mmol, 70.0 mg) using a catalyst composed of Pd\(_2\)(dba)\(_3\) (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), H\(_2\)O (0.40 mmol, 7 μL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (43.0 mg, 65%) as a bright yellow solid, mp 153–157 °C: \([\alpha]^{23}_D \approx -75.4 \text{ (c 1.10, CH}_2\text{Cl}_2); \] \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 8.22 (d, \(J = 9.3 \text{ Hz}, 2\)H), 7.88 (d, \(J = 9.3 \text{ Hz}, 2\)H), 7.14–7.08 (m, 2H), 7.01 (app. t, \(J = 8.6 \text{ Hz}, 2\)H), 4.58–4.51 (m, 1H), 3.49 (app. t, \(J = 9.0 \text{ Hz}, 1\)H), 3.24 (dd, \(J = 3.1, 9.2 \text{ Hz}, 1\)H), 3.06 (dd, \(J = 3.3, 14.0 \text{ Hz}, 1\)H), 2.86–2.75 (m, 1H), 2.77 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 162.1 (d, \(J = 245.0 \text{ Hz}), 156.6 145.0, 142.0, 131.1 (d, \(J= 3.5 \text{ Hz}), 130.7 (d, \(J = 8.0 \text{ Hz}), 125.1, 117.7, 115.8 (d, \(J = 21.3 \text{ Hz}), 53.4, 48.2, 36.8, 30.7; \) IR (film) 1717 cm\(^{-1}\). MS (Cl) 330.1258 (330.1248 calcd for C\(_{17}\)H\(_{16}\)F\(_3\)N\(_3\)O\(_3\), M + H\(^+\)). The enantiopurity was determined to be 94% ee by chiral HPLC
(-)-(4S)-4-(4-Chlorobenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (2l). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-bromochlorobenzene (0.40 mmol, 76.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), H$_2$O (0.40 mmol, 7 µL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (51.2 mg, 74%) as a bright yellow solid, mp 144–147 °C: [α]$^D_{23}$ –72.9 (c 0.81, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.24 (d, J = 9.3 Hz, 2H), 7.78 (d, J = 9.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 4.57–4.50 (m, 1H), 3.48 (app. t, J = 9.0 Hz, 1H), 3.23 (dd, J = 3.1, 9.1 Hz, 1H), 3.08 (dd, J = 3.3, 14.0 Hz, 1H), 2.85–2.78 (m, 1H), 2.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.6, 144.9, 142.1, 133.8, 133.3, 130.5, 129.0, 125.1, 117.7, 53.3, 48.2, 37.0, 34.4; IR (film) 1716 cm$^{-1}$. MS (Cl) 346.0956 (346.0953 calcd for C$_{17}$H$_{16}$ClN$_3$O$_3$, M + H$^+$). The enantiopurity was determined to be 93% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 195 nm, RT= 12.5 and 22.7 min).
(−)-(4S)-1-Methyl-4-(naphthalen-2-ylmethyl)-3-(4-nitrophenyl)imidazolidin-2-one (2n). The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 2-bromonaphthalene (0.40 mmol, 82.8 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (51.3 mg, 71%) as a bright yellow solid, mp 152–155 °C: [α]$^{23}_D$ −116.7 (c 0.74, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, $J = 9.1$ Hz, 2H), 7.86–7.78 (m, 5H), 7.62 (s, 1H), 7.54–7.46 (m, 2H), 7.28 (d, $J = 8.4$ Hz, 1H), 4.68–4.61 (m, 1H), 3.46 (app. t, $J = 9.2$ Hz, 1H), 3.36–3.28 (m, 2H), 2.93 (dd, $J = 9.3$, 13.9 Hz, 1H), 2.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 145.1, 142.0, 133.4, 133.0, 132.4, 128.7, 128.0, 127.7, 127.4, 126.9, 126.5, 126.0, 125.0, 117.8, 53.6, 48.5, 37.9, 30.8; IR (film) 1715 cm$^{-1}$. MS (Cl) 362.1507 (362.1499 calcd for C$_{21}$H$_{19}$N$_3$O$_3$, M + H$^+$). The enantiopurity was determined to be 89% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 198 nm, RT= 9.4 and 17.4 min).
(−)-(4S)-1-Methyl-4-(4-morpholinobenzyl)-3-(4-nitrophenyl)imidazolidin-2-one (2o).

The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-(4-bromophenyl)morpholine (0.40 mmol, 96.8 mg) using a catalyst composed of \( \text{Pd}_2(\text{dba})_3 \) (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), \( \text{H}_2\text{O} \) (0.40 mmol, 7 µL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (63.4 mg, 80%) as a bright yellow solid, mp 125–129 °C: \([\alpha]^{23}_D \) −91.0 (c 0.97, \( \text{CH}_2\text{Cl}_2 \)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.22 (d, \( J = 9.2 \text{ Hz} \), 2H), 7.78 (d, \( J = 9.2 \text{ Hz} \), 2H), 7.05 (d, \( J = 8.4 \text{ Hz} \), 2H), 6.86 (d, \( J = 8.4 \text{ Hz} \), 2H), 4.53–4.45 (m, 1H), 3.90–3.81 (m, 4H), 3.46 (app. t, \( J = 8.9 \text{ Hz} \), 1H), 3.27 (dd, \( J = 2.9, 9.2 \text{ Hz} \), 1H), 3.18–3.08 (m, 4H), 3.04 (dd, \( J = 3.2, 14.1 \text{ Hz} \), 1H), 2.81 (s, 3H), 2.72 (dd, \( J = 8.8, 14.0 \text{ Hz} \), 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 156.7, 150.4, 145.2, 141.9, 130.0, 126.6, 125.0, 117.7, 115.9, 67.1, 53.8, 49.3, 48.4, 36.8, 30.8; IR (film) 1717 cm\(^{-1}\). MS (Cl) 397.1872 (397.1870 calcd for \( \text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_4 \) M+H\(^+\)). The enantiopurity was determined to be 87% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 195 nm, RT= 25.7 and 33.0 min).
(-)-(4S)-4-(4-Methoxybenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (2p).

The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (0.20 mmol, 47.0 mg) and 4-bromoanisole (0.40 mmol, 74.8 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012 mmol 6.1 mg), TFA (0.08 mmol, 6 μL) as an additive, a reaction temperature of 115 °C and a reaction time of 18 h. This procedure afforded the title compound (55.3 mg, 81%) as a bright yellow solid, mp 110–113 °C: [α]$^2_{D}^{23}$ −71.3 (c 0.98, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.22 (d, $J$ = 9.2 Hz, 2H), 7.79 (d, $J$ = 9.4 Hz, 2H), 7.06 (d, $J$ = 8.5 Hz, 2H), 6.85 (d, $J$ = 8.5 Hz, 2H), 4.52–4.48 (m, 1H), 3.77 (s, 3H), 3.46 (app. t, $J$ = 8.9 Hz, 1H), 3.26 (dd, $J$ = 3.2, 9.0 Hz, 1H), 3.04 (dd, $J$ = 3.4, 14.1 Hz, 1H), 2.79 (s, 3H), 2.74 (dd, $J$ = 8.9, 14.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.8, 156.7, 145.2, 141.9, 130.2, 127.3, 125.0, 117.7, 114.3, 55.3, 53.7, 48.3, 36.8, 30.8; IR (film) 1717 cm$^{-1}$. MS (Cl) 342.1457 (342.1448 calcd for C$_{18}$H$_{19}$N$_3$O$_4$, M + H$^+$). The enantiopurity was determined to be 90% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 195 nm, RT= 14.1 and 25.9 min.)
(−)-(4S)-4-(3-Methoxybenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one  (2q).
The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-
nitrophenyl)urea (0.20 mmol, 47.0 mg) and 3-bromoanisole (0.40 mmol, 74.8 mg) using
a catalyst composed of Pd$_2$(dba)$_3$ (0.004 mmol, 3.7 mg) and (S)-Siphos-PE (0.012
mmol 6.1 mg), a reaction temperature of 115 °C and a reaction time of 18 h. This
procedure afforded the title compound (51.2 mg, 75%) as a bright yellow solid, mp 110–
114 °C: [α]$^{23}_D$ −94.2 (c 0.73, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J$ = 9.1 Hz,
2H), 7.77 (d, $J$ = 9.3 Hz, 2H), 7.23 (t, $J$ = 8.0 Hz, 1H), 6.78 (d, $J$ = 8.4 Hz, 1H), 6.73 (d, $J$
= 7.6 Hz, 1H), 6.65 (s, 1H), 4.56–4.48 (m, 1H), 3.76 (s, 1H), 3.44 (app. t, $J$ = 9.0 Hz,
1H), 3.26 (dd, $J$ = 2.9, 9.2 Hz, 1H), 3.08 (dd, $J$ = 3.3, 13.9 Hz, 1H), 2.79 (s, 3H), 2.73
(dd, $J$ = 9.0, 13.9 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.9, 156.7, 145.1, 141.9,
137.1, 129.9, 125.0, 121.4, 117.6, 115.4, 112.0, 55.2, 53.5, 48.4, 37.7, 30.8; IR (film)
1716 cm$^{-1}$. MS (Cl) 342.1461 (342.1448 calcd for C$_{18}$H$_{19}$N$_3$O$_4$, M + H$^+$). The
enantiopurity was determined to be 83% ee by chiral HPLC analysis (chiralcel ADH, 25
cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 195 nm, RT= 12.6 and 19.6 min).
(+)-(E,5S)-4-(3-Methyl-2-oxo-5-(3-(trimethylsilyl)allyl)imidazolidin-1-yl)benzonitrile (2r). The general procedure was employed for the coupling of 1-allyl-3-(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 2-bromovinyltrimethylsilane (0.20 mmol, 35.8 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound (20.0 mg, 64%) as a light orange solid, mp 130–133 °C: $[\alpha]_D^{23}$ +6.4 (c 0.50, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J$ = 9.0 Hz, 2H), 7.59 (d, $J$ = 8.8 Hz, 2H), 5.87 (dt, $J$ = 6.2, 18.5 Hz, 1H), 5.76 (d, $J$ = 18.7 Hz, 1H), 4.35 (m, 1H), 3.56 (app. t, $J$ = 9.0 Hz, 1H), 3.23 (dd, $J$ = 3.4, 9.1 Hz, 1H), 2.88 (s, 3H) 2.53 (m, 1H), 2.38 (m, 1H) 0.04 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.6, 143.1, 138.8, 136.5, 133.0, 127.5, 119.1, 118.6, 105.0, 51.6, 48.8, 38.9, 30.8, −1.4; IR (film) 1702 cm$^{-1}$; MS (Cl) 314.1685 (314.1683 calcd for C$_{17}$H$_{23}$N$_3$O$\text{Si}$, M + H$^+$). The enantiopurity was determined to be 86% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 200 nm, RT= 3.9 and 5.1 min).
(−)-(5S)-4-{3-Methyl-2-oxo-5-[4-(trifluoromethyl)benzyl]imidazolidin-1-yl}benzonitrile (2s). The general procedure was employed for the coupling of 1-allyl-3-(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 4-bromobenzotrifluoride (0.20 mmol, 45.0 mg), using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), water (3.5 μL, 0.20 mmol) as an additive, a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound (20.7 mg, 58%) as a light orange solid, mp 120–124 °C: [α]$^{23}_D$ −29.5 (c 1.12, CH$_2$Cl$_2$); $^1$H NMR (700 MHz, CDCl$_3$) δ 7.72 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.56-4.52 (m, 1H), 3.46 (app. t, J = 9.0 Hz, 1H), 3.20 (dd, J = 3.4, 9.0 Hz, 1H), 3.13 (dd, J = 3.3, 14.1 Hz, 1H), 2.97 (dd, J = 8.7, 14.0 Hz, 1H), 2.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 142.9, 139.7, 133.2, 129.7 (q, 32.4 Hz), 129.6, 125.8(q, 3.8 Hz), 124.0 (q, 272.0 Hz), 119.1, 118.7, 105.5, 53.0, 48.4, 37.5, 30.7 ; IR (film) 1717 cm$^{-1}$; MS (Cl) 360.1322 (360.1318 calcd for C$_{19}$H$_{16}$F$_3$N$_3$O, M + H$^+$). The enantiopurity was determined to be 77% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 200nm, RT= 8.9 and 16.6 min).

(−)-5S-4-{3-Methyl-2-oxo-5-[4-(trifluoromethyl)benzyl]imidazolidin-1-yl}benzonitrile. (2s): The general procedure was employed for the coupling of 1-allyl-3-
(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 4-iodobenzotrifluoride (0.20 mmol, 54.4 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), water (3.5 μL, 0.20 mmol) as an additive, a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound (27.9 mg, 77%) as a light orange oil. The enantiopurity was determined to be 80% ee by chiral HPLC analysis. Spectroscopic data were identical to those reported above.

(-)-(5S)-4-[3-Methyl-5-(4-methylbenzyl)-2-oxoimidazolidin-1-yl]benzonitrile (2t). The general procedure was employed for the coupling of 1-allyl-3-(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 4-bromotoluene (0.20 mmol, 34.2 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound (26.3 mg, 86%) as a light orange solid, mp 123–126 °C: [α]$_D^{23}$ –55.7 (c 0.90, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 4.51–4.45 (m, 1H), 3.44 (app. t, J = 9.0 Hz, 1H), 3.26 (dd, J = 3.7, 9.2 Hz, 1H), 3.09 (dd, J = 3.4, 13.9 Hz, 1H), 2.82 (s, 3H) 2.72 (dd, J = 9.3, 13.9 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz,
CDCl$_3$ $\delta$ 156.9, 143.2, 136.9, 133.1, 132.5, 129.5, 129.0, 119.2, 118.5, 105.0, 53.5, 48.5, 37.2, 30.8, 21.0; IR (film) 1712 cm$^{-1}$; MS (Cl) 306.1608 (306.1601 calcd for C$_{19}$H$_{19}$N$_3$O, M + H$^+$). The enantiopurity was determined to be 85% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, $\lambda$ 198 nm, RT= 5.4 and 8.6 min).

(--)-(5S)-4-[3-Methyl-5-(4-methylbenzyl)-2-oxoimidazolidin-1-yl]benzonitrile (2t): The general procedure was employed for the coupling of 1-allyl-3-(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 4-iodotoluene (0.20 mmol, 43.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0 mg), a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound (27.2 mg, 89%) as a light orange oil. The enantiopurity was determined to be 73% ee by chiral HPLC analysis. Spectroscopic data were identical to those reported above.

(--)-(5S)-4-[5-(4-Methoxybenzyl)-3-methyl-2-oxoimidazolidin-1-yl]benzonitrile (2u). The general procedure was employed for the coupling of 1-allyl-3-(4-cyanophenyl)-1-methylurea (0.10 mmol, 21.5 mg) and 4-bromoanisole (0.20 mmol, 37.4 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol,
3.0 mg), a reaction temperature of 120 °C and a reaction time of 14 h. This procedure afforded the title compound in (23.5 mg, 73%) as a light orange solid, mp 87–91 °C: $\text{[}\alpha\text{]}^{23}_{D} -52.9 \,(c \,0.37, \text{CH}_2\text{Cl}_2)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 9.0$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 4.46 (m, 1H), 3.79 (s, 3H), 3.43 (app. t, $J = 9.0$ Hz, 1H), 3.24 (dd, $J = 3.3$, 9.2 Hz, 1H), 3.04 (dd, $J = 3.3$, 14.0 Hz, 1H), 2.80 (s, 3H) 2.71 (dd, $J = 9.0$, 14.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.4, 156.9, 143.2, 133.1, 130.2, 127.5, 118.5, 114.2, 105.0, 55.3, 53.5, 48.5, 36.7, 30.8; IR (film) 1711 cm$^{-1}$; MS (Cl) 322.1548 (322.1550 calcd for C$_{19}$H$_{19}$N$_3$O$_2$, M + H$^+$).

The enantiopurity was determined to be 82% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, $\lambda$ 198 nm, RT= 12.3 and 23.3 min).

(+-)(4S)-4-[4-(tert-Butyl)benzyl]-1,4-dimethyl-3-(4-nitrophenyl)imidazolidin-2-one (5): The general procedure was employed for the coupling of 1-methyl-1-(2-methylallyl)-3-(4-nitrophenyl)urea (0.10 mmol, 24.9 mg) and 4-bromo-tert-butylbenzene (0.20 mmol, 42.6 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol, 3.0mg), a reaction temperature of 135 °C and a reaction time of 18 h. This procedure afforded the title compound (27.5 mg, 72%) as a yellow oil: $\text{[}\alpha\text{]}^{23}_{D} +70.2 \,(c \,0.90, \text{CH}_2\text{Cl}_2)$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (d, $J = 9.1$ Hz, 2H), 7.54 (d, $J = 9.1$ Hz, 2H), 7.06 (dd, $J = 9.1$, 2H), 6.85 (dd, $J = 9.1$, 2H), 5.04 (d, $J = 9.1$ Hz, 2H), 4.47 (m, 1H), 4.00 (s, 3H), 3.73 (app. t, $J = 9.1$ Hz, 1H), 3.24 (dd, $J = 3.3$, 9.2 Hz, 1H), 3.04 (dd, $J = 3.3$, 14.0 Hz, 1H), 2.80 (s, 3H) 2.71 (dd, $J = 9.1$, 14.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.4, 156.9, 143.2, 133.1, 130.2, 127.5, 118.5, 114.2, 105.0, 55.3, 53.5, 48.5, 36.7, 30.8; IR (film) 1711 cm$^{-1}$; MS (Cl) 322.1548 (322.1550 calcd for C$_{19}$H$_{19}$N$_3$O$_2$, M + H$^+$).
Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 3.49 (d, J = 9.1 Hz, 1H), 3.11 (d, J = 13.5 Hz, 1H), 3.23 (d, J = 8.8 Hz, 1H), 2.81 (d, J = 14.4 Hz, 1H), 2.74 (s, 3H), 1.47, (s, 3H), 1.29 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.0, 150.2, 144.5, 144.3, 132.3, 129.7, 125.6, 125.4, 124.4, 61.5, 56.3, 44.2, 34.5, 313, 30.6, 25.1; IR (film) 1716 cm$^{-1}$; MS (Cl) 382.2133 (382.2125 calcd for C$_{22}$H$_{27}$N$_3$O$_3$, M + H$^+$). The enantiopurity was determined to be 76% ee by chiral HPLC analysis (ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 198 nm, RT= 7.5 and 7.9 min.)

Deuterium Labeling Studies:

(Z)-1-(3-d-Allyl)-1-methyl-3-(4-nitrophenyl)urea ((Z)-d-1f).$^2$ A flame dried round bottom flask equipped with a stir bar was cooled to rt under a stream of N$_2$ and charged with N-methylallylamine (5.0 mmol, 0.47 mL) and Et$_2$O (10 mL). The resulting solution was cooled to −42 °C using a CO$_2$/CH$_3$CN bath and stirred for 5 min. A solution of n-BuLi in hexanes (3.12 mL, 1.6 M, 5 mmol) was added slowly and the resulting mixture was stirred at −42 °C for 20 min. A solution of t-BuLi in pentane (3.50 mL, 1.4 M, 5 mmol) was added slowly and the resulting solution was stirred at −42 °C for 30 min. The CO$_2$/CH$_3$CN bath was replaced with a brine/ice bath and the reaction mixture was allowed to slowly warm to room temperature as the ice melted. The bath was removed and the mixture was stirred at rt for 1 h. The reaction mixture was then cooled to −78 °C and D$_2$O (1.8 mL, 100 mmol) from freshly cracked ampoules was slowly added. The
resulting mixture was warmed to rt and stirred overnight. The reaction mixture was cooled to 0 °C, quenched with H₂O (2 mL) and transferred to a separatory funnel. The mixture was extracted with Et₂O (2 x 5 mL) and the combined organic layers were dried over anhydrous Na₂SO₄ and filtered to afford a solution of (Z)-N-methyl-3-deuterioallylamine. The solution was transferred to a round bottom flask and cooled to 0 °C. A solution of 4-nitrophosphylisocyanate (3.63 mmol, 596 mg) in CH₂Cl₂ (4 mL) was slowly added and the resulting mixture was warmed to rt and stirred for 5 h. The reaction mixture was then concentrated in vacuo and the crude product was purified by flash chromatography on silica gel to afford the title compound as (315 mg, 37% yield, >95% deuterium incorporation) a yellow solid, mp 80–83 °C. ^1H NMR (700 MHz, CDCl₃) δ 8.12 (d, J = 9.2 Hz, 2H), 7.51 (d, J = 9.2 Hz, 2H), 6.88 (s, br, 1H), 5.87–5.82 (m, 1H), 5.27 (d, J = 10.4 Hz, 1H), 3.98 (d, J = 5.3 Hz, 2H), 3.03 (s, 3H); ^13C NMR (175 MHz, CDCl₃) δ 154.5, 145.5, 142.3, 132.7, 125.0, 118.4, 117.2 (t, J = 23.8 Hz), 51.6, 34.8; IR (film) 1652 cm⁻¹. MS (Cl) 237.1099 (237.1092 calcd for C₁₁H₁₂D₁N₃O₃, M + H⁺).

(--)-(1'R,4S)-1'-Deuterio-4-[4-(tert-butyl)benzyl]-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (d-2f). The general procedure was employed for the coupling of (Z)-1-(3-allyl)-1-methyl-3-(4-nitrophenyl)urea (0.10 mmol, 23.6 mg) and 4-bromo-tert-butylbenzene (0.20 mmol, 42.6 mg) using a catalyst composed of Pd₂(dba)₃ (0.002 mmol, 1.8 mg) and (S)-Siphos-PE (0.006 mmol 3.0 mg), a reaction temperature
of 115 °C, and a reaction time of 18 h. This procedure afforded the title compound (32.1 mg, 85%) as a bright yellow solid, mp 110–113 °C, [α]$_{D}^{23}$ -104 (c 1.00, CH$_2$Cl$_2$). This material was judged to be a 7:1 mixture of diastereomers by $^1$H NMR analysis. Data are for the major isomer: $^1$H NMR (700 MHz, CDCl$_3$) δ 8.22 (d, $J$ = 8.9 Hz, 2H), 7.78 (d, $J$ = 8.9 Hz, 2H), 7.34 (d, $J$ = 7.8 Hz, 2H), 7.09 (d, $J$ = 8.2 Hz, 2H), 4.54–4.50 (m, 1H), 3.48 (app. t, $J$ = 8.7 Hz, 1H), 3.29 (dd, $J$ = 2.6, 9.0 Hz, 1H), 3.09 (d, $J$ = 3.2 Hz, 0.12 H), 2.74 (d, $J$ = 9.0 Hz, 0.88 H), 2.83 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (175 MHz, CDCl$_3$) δ 156.7, 150.3, 145.2, 141.9, 132.4, 128.8, 125.8, 125.0, 117.7, 53.7, 48.6, 37.0 (t, $J$ = 17.7 Hz), 34.5, 31.3, 30.8; IR (film) 1717 cm$^{-1}$. MS (Cl) 369.2034 (369.2031 calcd for C$_{21}$H$_{24}$D$_3$N$_3$O$_3$, M + H$^+$). The enantiopurity was determined to be 91% ee by chiral HPLC analysis (ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 198 nm, RT= 6.3 and 9.5 min). The 1'R,4S relative stereochemistry was assigned on the basis of comparison of NMR data to those obtained for a sample of the title compound prepared using a catalyst composed of Pd$_2$(dba)$_3$ and DPE-Phos, which has previously been shown to effect the syn-carboamination of N-allylurea derivatives.$^1$

Discussion of Mechanism of Diastereomer Formation in the Reaction of (Z)-d-1f

The formation of the minor diastereomer in the reaction of (Z)-d-1f is likely due to competing β-hydride elimination processes, as we have previously observed in related tetrahydrofuran-forming reactions.$^{[4]}$ As shown below in Scheme S1, intermediate S1 (generated via oxidative addition of the aryl bromide to Pd(0) followed by deprotonation and transmetallation of the substrate) is formed from (Z)-d-1f. The syn-migratory insertion of the alkene into the Pd–N bond affords S2, which can undergo reductive
elimination to yield (1'R,4S)-d-2m. However, if this reductive elimination is relatively slow, S2 can undergo sigma bond rotation to S2a followed by syn-β-hydride elimination to afford S3. Reinsertion of the alkene into the Pd–H bond with the opposite regiochemistry provides S4, which can undergo sigma bond rotation to S4a. The syn-β-hydride elimination of H from S4a provides S5, which can undergo reinsertion of the alkene into the Pd–H bond to give S6. Reductive elimination from S6 then affords the minor diastereomer (1'S,4S)-d-2m. No migration of the deuterium atom was observed, which is presumably a result of a kinetic isotope effect coupled with the statistical probability for β-H vs. β-D elimination.

Scheme S1. Mechanism of diastereomer formation in the reaction of (Z)-d-1f.
Deprotection of 2m and Assignment of Absolute Stereochemistry:

The absolute stereochemistry of the urea products was assigned by deprotection of 2m (prepared via Pd-catalyzed carboamination of 1f) to urea 6. The optical rotation of 6 was of the same sign (−) as that of a separate sample of 6 prepared from L-phenylalanine as described below.

(--)-(4S)-4-Benzyl-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (2m): The general procedure was employed for the coupling of 1-allyl-1-methyl-3-(4-nitrophenyl)urea (1.0 mmol, 235.2 mg) and bromobenzene (1.2 mmol, 188.4 mg) using a catalyst composed of Pd$_2$(dba)$_3$ (0.02 mmol, 18.0 mg) and (S)-Siphos-PE (0.06 mmol, 30.0 mg), a reaction temperature of 115 °C, and a reaction time of 18 h. This procedure afforded the title compound (256.9 mg, 83%) as a bright yellow solid, mp 125–128 °C: [α]$^\text{D}$ $-108.9$ (c 1.22, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.24 (d, J = 9.3 Hz, 2H), 7.80 (d, J = 9.3 Hz, 2H), 7.33 (t, J = 6.9 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 7.1 Hz, 2H), 4.58–4.52 (m, 1H), 3.47 (app. t, J = 8.8 Hz, 1H), 3.28 (dd, J = 2.9, 9.2 Hz, 1H), 3.14 (dd, J = 3.2, 13.9 Hz, 1H), 2.83–2.77 (m, 1H), 2.81 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 156.7, 145.1, 142.0, 135.5, 129.2, 128.9, 127.3, 125.0, 117.7, 53.7, 48.4, 37.7, 30.8; IR (film) 1717 cm$^{-1}$; MS (Cl) 312.1347 (312.1343 calcd for C$_{17}$H$_{17}$N$_3$O$_3$, M + H$^+$. The
enantiopurity was determined to be 89% ee by chiral HPLC analysis (chiralcel ADH, 25 cm x 4.6 mm, 15% IPA/Hexanes, 1.5 mL/min, λ 198 nm, RT= 10.5 and 17.1 min).

(-)-(4S)-4-Benzyl-1-methylimidazolidin-2-one (6). A glass microwave tube equipped with a stir bar was charged with 4-Benzyl-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (77.8 mg, 0.25 mmol,), 10% Pd/C (38.9 mg, 5% w/w Pd), ethyl acetate (2 mL) and methanol (1 mL). The tube was placed into a stainless steel bomb that was pressurized with H₂ to 50 psi and the reaction mixture was then stirred at rt for 12 h. The reaction vessel was then depressurized and the mixture was filtered through a pad of celite. The celite was washed with methanol (25 mL) and the combined organic solutions were concentrated in vacuo. The crude product from this reaction was dissolved in CH₂Cl₂ (0.7 mL) and transferred to a flame dried Schlenk tube equipped with a stir bar that had been cooled under a stream of nitrogen. Acetic anhydride (28 µL, 0.30 mmol) was added to the flask and the resulting solution was stirred at rt for 5 h. A solution of saturated aqueous Na₂CO₃ (5 mL) was added to the reaction vessel and the resulting mixture was transferred to a separatory funnel. The mixture was extracted with CH₂Cl₂ (3 x 10 mL) and the combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product from this reaction was placed into a round bottom flask equipped with a stir bar and dissolved in CH₃CN (3.5 mL) and
H₂O (0.70 mL). The mixture was cooled to 0 °C, stirred for 5 min, then ceric ammonium nitrate (1.13 mmol, 618.0 mg) was added in one portion. The resulting mixture was stirred at 0 °C for 25 min then saturated aqueous sodium sulfite (6 mL) was added. The mixture was transferred to a separatory funnel and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated aqueous NaHCO₃ (5 mL) and brine (5 mL) then dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to afford the title compound (41.6 mg, 88% overall yield) as a brown oil, [α]²³Ð –27.0 (c 1.0, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, J = 7.1 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.1 Hz, 2H), 4.82–4.52 (s, br, 1H), 3.85 (m, 1H), 3.47 (app. t, J = 8.6 Hz, 1H), 3.13 (dd, J = 6.1, 8.8 Hz, 1H), 2.81 (app. d, J = 7.1 Hz, 2H), 2.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.9, 137.1, 129.0, 128.8, 126.9, 52.7, 51.1, 42.0, 30.5; IR (film) 1699 cm⁻¹; MS (Cl) 191.1181 (191.1179 calcd for C₁₁H₁₄N₂O, M + H⁺). The enantiopurity was determined to be 85% ee by chiral HPLC analysis (Lux Amylose-2, 25 cm x 4.6 mm, 10% IPA/Hexanes, 1.0 mL/min, λ 210 nm, RT= 21.3 and 22.7 min).

(−)-(4S)-4-Benzyl-1-methylimidazolidin-2-one (6) A flame-dried round bottomed flask equipped with a stirbar was cooled under a stream of nitrogen and charged with (S)-N¹-methyl-3-phenylpropane-1,2-diamine (100.0 mg, 0.60 mmol) and THF (1 mL). Solid CDI (90.0 mg, 0.56 mmol) was added and the resulting mixture was heated to 60 °C with stirring for 12 h. The reaction mixture was then cooled to rt and the solvent was
removed in vacuo. The product was purified by flash chromatography on silica gel to afford the title compound (32.0 mg, 30% yield); [α]$^2_{D}$ −37.2 (c 0.90, CH$_2$Cl$_2$). The spectroscopic properties of this compound were identical to that of compound 6. The enantiopurity was determined to be 97% ee by chiral HPLC analysis (Lux Amylose-2, 25 cm x 4.6 mm, 10% IPA/Hexanes, 1.0 mL/min, λ 210 nm, RT= 21.3 and 22.7 min).

References


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Data Acquired: 6/6/2012 11:32:16 AM
Data Processed: 6/6/2012 11:58:47 AM

<Chromatogram>

Peak Table

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: BAH-H27/2c
Sample ID: <SAMPLE>
Tray #: 1
Vial #: 1
Injection Volume: 1 µL
Data File Name: BAH-H27/2c Iod
Method File Name: Cyclic Urine Method Iod
Batch File Name: -
Report File Name: Datafooter
Data Acquired: 7/2/2012 2:24:18 PM
Data Processed: 7/2/2012 2:37:21 PM

Chromatogram

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Carbon-13
Sample Name:
Data Collected on:
70 Chem.Lab. Mclm.edu
Sample directory:
File Name: SAB-1124carbon
Pulse Sequence: CARPH (150us)
Solvent: dmsol
Data collected on: May 19 2012
**** Shimadzu LCsolution Analysis Report ****

Acquired by: Admin
Sample Name: RAC-BAHI-II-154-ADH-15%MIPA-1.5ml_min
Sample ID: <SAMPLE>
Tray#: 1
Vial #: 1
Injection Volume: 1.0 µL
Data File Name: RAC-BAHI-II-154-ADH-15%MIPA-1.5ml_min.lcd
Method File Name: Cyclic Urea Method_1.0m
Batch File Name: 
Report File Name: Default
Data Acquired: 6/6/2012 9:42:40 AM
Data Processed: 6/6/2012 10:43:59 AM

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PDA Ch1 195nm-440nm

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### Shimadzu LCsolution Analysis Report ###

- **Acquired by:** Admin
- **Sample Name:** CHIRAL-BAH-II-161-ADH-15%IPA-1.5ml_min.lcd
- **Sample ID:** <SAMPLE>
- **Tray #:** 1
- **Vial #:** 1
- **Injection Volume:** 10μL
- **Data File Name:** CHIRAL-BAH-II-161-ADH-15%IPA-1.5ml_min.lcd
- **Method File Name:** Cyclic Urea Method.lcm
- **Batch File Name:** Default.lcm
- **Report File Name:** Default.lcm
- **Data Acquired:** 6/6/2012 6:46:19 PM
- **Data Processed:** 6/6/2012 6:04:50 PM

----<Chromatogram>----

![Chromatogram](image)

---

### PeakTable (PDA Ch1 198nm 4mm) ---

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: RAC-BAHIII-760(1)-ADH-15%IPA-1.5mL/min
Sample ID: <SAMPLE>
Tray#: 1
Val# 1
Injection Volume: 1.0 mL
Data File Name: RAC-BAHIII-760(1)-ADH-15%IPA-1.5mL/min ldc
Method File Name: Cyclic Urea Method Ion
Batch File Name: 
Report File Name: Default for
Data Acquired: 1/30/2012 4:42:56 PM
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### Shimadzu LCsolution Analysis Report

- **Acquired by:** Admin
- **Sample Name:** CHIRAL-BAH-II-107(III)-ADH-15%/IPA-1.5ml_min._lod
- **Sample ID:** <SAMPLE>
- **T:0**
- **V:1**
- **Injection Volume:** 1.0 mL
- **Data File Name:** CHIRAL-BAH-II-107(III)-ADH-15%/IPA-1.5ml_min._lod
- **Method File Name:** Cycloic Urea Method_om
- **Batch File Name:**
- **Report File Name:** Default
- **Data Acquired:** 2020/07/12 12:57:09 PM
- **Data Processed:** 2020/07/12 8:16:12 PM

#### Chromatogram

![Chromatogram Image]

#### Peak Table

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1. PDA Multi 1: 198nm-4nm
2f (from 4-iodo-tert-butylbenzene)
== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: CHIRAL-BA-II-50(l)-AD-15%/IPA-1.50ml_min
Sample ID: <SAMPLE>
Tray#: 1
Valve#: 1
Injection Volume: 1.0 mL
Data File Name: CHIRAL-BA-II-50(l)-AD-15%/IPA-1.50ml_min.lcd
Method File Name: Cyclic-Urea Method ldm
Batch File Name: 
Report File Name: Default
Data Acquired: 2/13/2012 4:04:52 PM
Data Processed: 2/13/2012 4:38:11 PM

2g (without H2O)
== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: CHIRAL-BAH-III-50(II)-ACN-15%IPA-1.50mL_min.lcd
Sample ID: <SAMPLE>
Test #: 1
Visit #: 1
Injection Volume: 1 µL
Data File Name: CHIRAL-BAH-III-50(II)-ACN-15%IPA-1.50mL_min.lcd
Method File Name: Cyclic Urea Method I
Batch File Name:
Report File Name: Default.lcd
Data Acquired: 2/13/2012 4:36:55 PM
Data Processed: 2/13/2012 5:00:59 PM

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PDA Ch1 195nm 4am
Shimadzu LC Solution Analysis Report

Acquired by: Admin
Sample Name: BAH-III-120-1(2h)
Sample ID: <SAMPLE>
Tray#: 1
Vial #: 1
Injection Volume: 1 µL
Data File Name: BAH-III-120-1(2h).ldd
Method File Name: Cyclic Urca Method.ion
Report File Name: Default.ior
Data Acquired: 7/2/2012 4:42:41 PM
Data Processed: 7/2/2012 4:58:16 PM

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Peak Table

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==== Shimadzu LCsolution Analysis Report ====

Acquired by: Admin
Sample Name: racBAH-III-(S)-ADH-15%IPA-1.5ml_min1.los
Sample ID: <SAMPLE>
Tray#: 1
Valve: 1
Injection Volume: 1 uL
Data File Name: racBAH-III-(S)-ADH-15%IPA-1.5ml_min1.los
Method File Name: Cyclic Urea Method.los
Batch File Name: 
Report File Name: Default.los
Data Acquired: 2/16/2012 5:53:49 PM
Data Processed: 2/16/2012 6:11:00 PM

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PDA Ch1 195nm 4nm

PeakTable
== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: BAIII-125-II(2)
Sample ID: <SAMPLE>
Tray#: 1
Vial#: 1
Injection Volume: 1.0uL
Data File Name: BAIII-125-II(2).tdf
Method File Name: Cyclic-Urea-Method-1mm
Batch File Name: 
Report File Name: 
Data Acquired: 7/2/2012 3:23:41 PM
Data Processed: 7/2/2012 3:41:47 PM

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==== Shimadzu LCsolution Analysis Report ====  

Acquired by: Admin  
Sample Name: RAC-BAH-II-115-IVADH-15%IPA-1.5ml_min.1cd  
Sample ID: <SAMPLE>  
Tray #: 1  
Vial #: 1  
Injection Volume: 1.0 ml  
Data File Name: RAC-BAH-II-115-IVADH-15%IPA-1.5ml_min.1cd  
Method File Name: Cytox Urca Method.1m  
Batch File Name:  
Report File Name: Default.1r  
Data Acquired: 6/18/2012 1:11:20 PM  
Data Processed: 6/18/2012 3:21:23 PM

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Shimadzu LCsolution Analysis Report

Assayed by: Admin
Sample Name: CAH-III-93(I1)ACN-IPA-1.5mL_min1.txt
Sample ID: <SAMPLE>
Injection Volume: 10 µL
Data File Name: CAH-III-93(I1)ACN-IPA-1.5mL_min1.txt
Method File Name: Cyclic Urea Method Imon
Batch File Name: Default.txt
Report File Name: Default.txt
Data Acquired: 2/10/2012 02:23 PM
Data Processed: 2/10/2012 06:58 PM

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PDA Multi 1

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: CHIRAL-BAH-III-122-ADH-15%IPA-1.5mL_min_1od
Sample ID: <SAMPLE>
Tray #: 1
Vial #: 1
Injection Volume: 1.0 µL
Data File Name: CHIRAL-BAH-III-122-ADH-15%IPA-1.5mL_min_1od
Method File Name: Cyclic Urea Method.ltm
Batch File Name: 
Report File Name: Default.ltr
Data Acquired: 3/19/2012 2:39:49 PM
Data Processed: 3/19/2012 3:05:11 PM

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PeakTable

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: RAC-BAH-III-191(/)-ADH-15%/PA-1.5mL_min
Sample ID: <SAMPLE>
Tray#: 1
Val#: 1
Injection Volume: 1.0L
Data File Name: RAC-BAH-III-191(/)-ADH-15%/PA-1.5mL_min.lcd
Method File Name: Cyclic Urea Method.lcm
Batch File Name: 
Report File Name: Default.lcr
Data Acquired: 6/18/2012 12:04:41 PM
Data Processed: 6/18/2012 12:31:06 PM

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**** Shimadzu LCsolution Analysis Report ****

Acquired by: Admin
Sample Name: BAH-i-134-iii(2)
Sample ID: <SAMPLE>
Tray #: 1
Val #: 1
Injection Volume: 1.0 μL
Data File Name: BAH-i-134-iii(2).lcf
Method File Name: Cyclic Urea Method Icm
Batch File Name: Default.lcf
Data Acquired: 7/2/2012 5:00:23 PM
Data Processed: 7/2/2012 5:15:34 PM

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PDA Ch1 195nm 4nm
==== Shimadzu LCsolution Analysis Report ====

Acquired by:  Admin
Sample Name:  CHIRAL-BAH-II-178(II):ADH-15%IPA-1.5ml_min
Sample ID:  <Sample File>
Tray #:  1
Vial #:  1
Injection Volume:  1.0 µL
Data File Name:  CHIRAL-BAH-II-178(II):ADH-15%IPA-1.5ml_min
Method File Name:  Cyclic Urea Method. lom
Batch File Name:  Default. lom
Report File Name:  Default. lom
Data Acquired:  06/10/2012 1:05:47 PM
Data Processed:  06/10/2012 1:20:02 PM

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== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: BAHIII-147-2n
Sample ID: <SAMPLE>
Tray#: 1
Val#: 1
Injection Volume: 1 µL
Data File Name: BAHIII-147-2n.lod
Method File Name: Cyclic Urea Method IOM
Batch File Name: 
Report File Name: Data.lod
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PDA Multi 1

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: RAC-BAH-III-853-ACH-15%IPA-1.5mL_min
Sample ID: <SAMPLE>
Tray #: 1
Vial #: 1
Injection Volume: 1 uL
Data File Name: RAC-BAH-III-893-ACH-15%IPA-1.5mL_min
Method File Name: Cyclic Urea Method.tsm
Batch File Name: 
Report File Name: Default
Data Acquired: 6/18/2012 1:26:15 PM
Data Processed: 6/18/2012 2:00:01 PM

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PDA Multi 1

PDA Ch1 195nm 4mm

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: CHIRAL BAH-III-108(IV)-ADH-15%/PA-1.5mL_min
Sample ID: <SAMPLE>
Tray#: 1
Val#: 1
Injection Volume: 1 uL
Data File Name: CHIRAL BAH-III-108(IV)-ADH-15%/PA-1.5mL_min.lod
Method File Name: Cyclohexane Method. txt
Batch File Name: 
Report File Name: Default lod
Data Acquired: 6/15/2012 17:37:12
Data Processed: 6/15/2012 17:37:12

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### Shimadzu LCsolution Analysis Report

**Acquired by:** Adrin  
**Sample Name:** RAC-BAH-III-54(l)-ADH-15%IPA-1.5ml_minTRY3  
**Sample ID:** SAMPLE  
**Tray #:** 1  
**Yel #:** 1  
**Injection Volume:** 1 µL  
**Data File Name:** RAC-BAH-III-54(l)-ADH-15%IPA-1.5ml_minTRY3.lod  
**Method File Name:** CycloUrea Methodหมวดหมู่  
**Batch File Name:** Default  
**Data Acquired:** 2/6/2012 5:05:14 PM  
**Data Processed:** 2/6/2012 5:30:02 PM

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**Chromatogram**

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![Chemical Structure](image)  

2p
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: CHIRAL-BAH III-104(II)-AD3-15%IPA-1.0mL/min std
Sample ID: <SAMPLE>
Tray#: 1
Val#: 1
Injection Volume: 1.0 mL
Data File Name: CHIRAL-BAH III-104(II)-AD3-15%IPA-1.0mL/min std
Method File Name: Cyclic Urea Method 1nm
Batch File Name: Default
Report File Name: Default
Data Acquired: 2/24/2012 4:19:50 PM
Data Processed: 2/24/2012 4:38:33 PM

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: isoBAH-III (V) ADH-15\%IPA-1.5mL/min
Sample ID: <SAMPLE>
 Tray: 1
 Valve: 1
 Injection Volume: 10 µL
 Data File Name: C:/LabSolutions/Data/B. Hopkins/isoBAH-III (V) ADH-15\%IPA-1.5mL/min
 Method File Name: Cyclic Urea Method 1.mn
 Batch File Name: 
 Report File Name: Default lor
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Area % | Height %
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48.359 | 36.124 |
100.000| 100.000|
Shimadzu LCsolution Analysis Report

Sample Name: CHIRAL BAH II-120(II)-ADH-15%IPA-1.5ml_min
Sample ID: <SAMPLE>
Injection Volume: 1 µL
Method File Name: Cyclic Urea Method Ion
Report File Name: Default.tsr

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=== Shimadzu LCsolution Analysis Report ===

Acquired by: Admin
Sample Name: rac-BHIII-21(l)-ADH-15MIPA-1.5mL_min
Sample ID: <SAMPLE>
Tray #: 1
Vial #: 1
Injection Volume: 1 µL
Data File Name: rac-BHIII-21(l)-ADH-15MIPA-1.5mL_min.lcd
Method File Name: Cyclic Urea Method.lam
Batch File Name: 
Report File Name: Default.cfg
Date Acquired: 6/10/2012 3:54:25 PM
Date Processed: 6/10/2012 4:02:42 PM

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6/12/2012 19:19:43 1 / 1
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: chilis-BAH-III-2(I)-ADH-15%IPA-1.5mL_min.1sid
Sample ID: <SAMPLE>
Tray #: 1
Val #: 1
Injection Volume: 1 mL
Method File Name: CyclicUreaMethod.1cm
Batch File Name: 
Report File Name: 
Data Acquired: 06/10/2012 4:04:38 PM
Data Processed: 06/10/2012 4:18:18 PM

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Peak Table

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== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: RAC-BAH-III-1456(II):ADH-15%IPA-1.5mL_min
Sample ID: <SAMPLE>
Tray #: 1
Val #: 1
Injection Volume: 1.0 μL
Data File Name: RAC-BAH-III-1456(II):ADH-15%IPA-1.5mL_min.lcd
Method File Name: Cyclic Urea Method-Ipm
Batch File Name: 
Report File Name: Default.lcd
Data Acquired: 5/4/2012 1:35:10 PM
Data Processed: 5/4/2012 2:02:04 PM

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== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: CHIRAL-BAH-II-145(III)-ADH-15%/IPA-1.5%/min.los
Sample ID: <SAMPLE>
Tray#: 1
Vial#: 1
Injection Volume: 1 uL
Data File Name: CHIRAL-BAH-II-145(III)-ADH-15%/IPA-1.5%/min.los
Method File Name: Cyclic-Urea Method.png
Batch File Name:
Report File Name: Default.los
Data Acquired: 6/4/2012 2:32:09 PM

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Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: CHIRAL-BAH-III-146(II)-AD-H-15%IPA-1.5mL_min_lod
Sample ID: SAMPLE
Tray#: 1
Val# : 1
Injection Volume: 1 µL
Data File Name: CHIRAL-BAH-III-146(II)-AD-H-15%IPA-1.5mL_min_lod
Method File Name: Cyclic_Urea_Method.lnm
Batch File Name: 
Report File Name: Default.lor
Data Acquired: 5/9/2012 12:08:35 PM
Data Processed: 5/9/2012 12:27:28 PM

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==== Shimadzu LC solution Analysis Report ====

Acquired by: Admin
Sample Name: CHIRAL-BAH-H-164(1a)-ADH-15%IPA-1.50mL_min
Sample ID: <SAMPLE>
Tray#: 1
Vial #: 1
Injection Volume: 1 μL
Data File Name: CHIRAL-BAH-H-164(1a)-ADH-15%IPA-1.50mL_min
Method File Name: Cyclic Urea Method Ion
Batch File Name: 
Report File Name: Default
Data Acquired: 8/27/2012 6:07:24 PM
Data Processed: 8/27/2012 6:27:38 PM

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PDA Multi

PDA Ch1 198nm 4nm

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7/1/2012 17:57:55 1 / 1
2t (w/ 4-iodotoluene)
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: RAC-BAH-II-6(1)-ADH-15%IPA-1.50mL_min
Sample ID: <SAMPLE>
Tray #: 1
Val #: 1
Injection Volume: 1.0L
Data File Name: RAC-BAH-II-6(1)-ADH-15%IPA-1.50mL_min.lod
Method File Name: Cyclic Urea Method.lcm
Batch File Name: 
Report File Name: Default.lcr
Data Acquired: 7/1/2012 6:03:55 PM
Data Processed: 7/1/2012 6:31:27 PM

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### Shimadzu LCsolution Analysis Report

- **Acquired by**: Admin
- **Sample Name**: CHIRAL-BAH-II(II)-ADH-15%/PA=1.50mL_min
- **Sample ID**: <SAMPLE>
- **Tray #**: 1
- **Vial #**: 1
- **Injection Volume**: 1 μL
- **Data File Name**: CHIRAL-BAH-II(II)-ADH-15%/PA=1.50mL_min
- **Method File Name**: Cyclic Urea Method.ion
- **Batch File Name**: Default
- **Data Acquired**: 7/1/2012 6:33:11 PM
- **Data Processed**: 7/1/2012 7:03:56 PM

![Chromatogram](image)

#### Peak Table

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Data Collected on: Jun 5 2012
Archive directory:
Sample directory:
File Name: Beam-III-117-III
Pulse Sequence: PROTON (xipul)
Solvent: acetic
Data collected on: Jun 5 2012

Carbon-13
Sample Name: Beam-III-117-III carbon
Data Collected on: Jun 5 2012
Archive directory:
Sample directory:
File Name: Beam-III-117-III carbon
Pulse Sequence: CARBON (xipul)
Solvent: acetic
Data collected on: Jun 5 2012
**** Shimadzu LCsolution Analysis Report ****

Acquired by: Admin  
Sample Name: RAC-GAH-III-192 ADH-15%IPA-1.5ml_min  
Sample ID: <SAMPLE>  
Tray #: 1  
Valve #: 1  
Injection Volume: 1 µL  
Data File Name: RAC-GAH-III-192 ADH-15%IPA-1.5ml_min  
Method File Name: Cyclic Urea Method  
Report File Name: Default  
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Data Processed: 6/15/2012 6:15:16 PM

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== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: CHIRAL-BAH-III-117(III)-ADH-15%IPA-1.5ml_min
Sample ID: <SAMPLE>
Tray #: 1
Val #: 1
Injection Volume: 1 μL
Data File Name: CHIRAL-BAH-III-117(III)-ADH-15%IPA-1.5ml_min lod
Method File Name: Cyclic Urea Method Iom
Batch File Name: 
Report File Name: Default lod
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Proton Spectrum
Sample Name:
Data Collected on: 2012-06-05
Archive directory:
Sample directory:
File Name: S119-164
Pulse Sequence: ROESY (x2pol)
Solvent: dme-d1
Data collected on: May 24 2012

Carbon-13
Sample Name:
Data Collected on: 2012-06-05
Archive directory:
Sample directory:
File Name: S119-164carbon
Pulse Sequence: CASBHR (x2pol)
Solvent: dme-d1
Data collected on: May 24 2012
== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: RAC-BAH-III-181-ADH-15%IPA-1.5ml_min
Sample ID: <SAMPLE>
Tray #: 1
Vial #: 1
Injection Volume: 1 ul.
Data File Name: RAC-BAH-III-181-ADH-15%IPA-1.5ml_min.lcd
Method File Name: Cyclic Lics Method Ion
Batch File Name: 
Report File Name: Default.lpr
Data Acquired: 5/17/2012 2:13:45 PM
Data Processed: 5/17/2012 2:40:16 PM

<Chromatogram>

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PDA Ch1 198nm 4nm

Peak Table
Shimadzu LCsolution Analysis Report

Acquired by: Admin  
Sample Name: BAHIII-164-d2f  
Sample ID: <SAMPLE>  
Tray #: 1  
Val # : 1  
Injection Volume : 1.0 uL  
Data File Name: BAHIII-164-d2f.lic  
Method File Name: Cyclic Urea Method .lic  
Batch File Name:  
Report File Name: Default .lic  
Data Acquired: 7/2/2012 6:48:32 PM  
Data Processed: 7/2/2012 5:59:45 PM

<Chromatogram>

Peak Table

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== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: RAC-BAH-HL-182-LUXAMYLOSE-10%IPA-1.0ml_min.txt
Sample ID: <SAMPLE>
Tray #: 1
Val #: 1
Injection Volume: 1.000 ml
Data File Name: RAC-BAH-HL-182-LUXAMYLOSE-10%IPA-1.0ml_min.txt
Method File Name: Cyclic Urea Method.ion
Batch File Name: 
Report File Name: Default for
Data Acquired: 06/11/2012 1:40:26 PM
Data Processed: 06/11/2012 2:30:15 PM

<Chromatogram>

![Chromatogram Image]

**PeakTable**

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Shimadzu LCsolution Analysis Report

6 (from L-phenylalanine)