Supporting Information

Nickel-Catalyzed Chemoselective Asymmetric Hydrogenation of \(\alpha, \beta\)-Unsaturated Ketoimines: An Efficient Approach to Chiral Allylic Amines

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I. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometers for $^1$H NMR and $^{13}$C NMR. CDCl$_3$ 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 $^1$H NMR and relative to CDCl$_3$ (77.16 ppm) for $^{13}$C NMR. Optical rotation was determined using a Perkin Elmer 343 polarimeter. HPLC analysis was conducted on an Agilent 1260 Series instrument. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh). All new products were further characterized by HRMS. A positive ion mass spectrum of sample was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source.
II. General procedure for the synthesis of \( \alpha, \beta \)-unsaturated ketoimines

Method A for the synthesis of \( \alpha, \beta \)-unsaturated ketoimines.

To a solution of 3-methyl-2-butenal in THF, PhMgBr (1.1 equiv) was added at 0 °C. The mixture was then stirred for 2 h at room temperature. Subsequently, the reaction was quenched with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford 3-methyl-1-phenylbut-2-en-1-ol.\(^{[1-2]}\)

To a solution of 3-methyl-1-phenylbut-2-en-1-ol in \( \text{Et}_2\text{O} \) was added MnO\(_2\) (10 equiv.). The mixture was then stirred for 12 h at room temperature. Subsequently, the reaction was filtered and the solvent was removed. The crude product was purified by column chromatography on silica gel to afford 3-methyl-1-phenylbut-2-en-1-one.\(^{[1-2]}\)

To a mixture of 3-methyl-1-phenylbut-2-en-1-one, methanesulfonamide (1 equiv.) and \( \text{Et}_3\text{N} \) (2.4 equiv.) in \( \text{CH}_2\text{Cl}_2 \) at 0 °C, was slowly added TiCl\(_4\) (1.2 equiv.). The
reaction mixture was initially stirred at 0 °C for 0.5 h and then at reflux temperature for 12 h. After complete consumption of the ketone substrate (monitored by TLC), the reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ and the combined organics were washed with water and dried over anhydrous Na₂SO₄. After removal of the organic solvent under vacuum, the residue was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired imine. The product can be further purified by recrystallization from ethanol. Substrates 1o were prepared through method A.

**Method B for the synthesis of α, β-unsaturated ketoimines.**

To a suspension of NaH (60 % dispersion in oil, 12.0 mmol) in THF (10 mL) was added a solution of triethyl phosphonoacetate (12.0 mmol) in THF (5 mL) under a nitrogen atmosphere at 0 °C. After being stirred at room temperature for 30 min, a solution of a corresponding ketone (10 mmol) in THF (5 mL) was added to the reaction mixture at 0 °C. After being further stirred at room temperature for 16 h, the reaction was quenched by adding saturated aqueous NaHCO₃ and diluted with EtOAc. The organic layer was separated and washed with brine, dried over MgSO₄ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding α, β-unsaturated ester. To a suspension of the α, β-unsaturated ester (3.0 mmol) obtained above and N,O-dimethylhydroxylamine hydrochloride (6.0 mmol) in THF (6.0 mL) was added dropwise i-PrMgCl (2.0 M solution in THF, 6.0 mmol) under nitrogen atmosphere at -5 to -10 °C. After being stirring at 0 °C for 30 min, the reaction was quenched by adding saturated aqueous NH₄Cl and diluted with EtOAc. The organic layer was separated and washed with brine, dried over MgSO₄ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding Weinreb amide.

To a solution of the Weinreb amide (1.0 mmol) obtained above in THF (2.0 mL) was added dropwise a solution of the corresponding Grignard reagent or lithium reagent.
(1.5 mmol) under nitrogen atmosphere at -30 °C. After being stirring at 0 °C for 30 min, the reaction was quenched by adding saturated aqueous NH₄Cl and diluted with EtOAc. The organic layer was separated and washed with brine, dried over MgSO₄ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the β, β-disubstituted enone.

To a mixture of β, β-disubstituted enone, methanesulfonamide (1 equiv.) and Et₃N (2.4 equiv.) in CH₂Cl₂ at 0 °C, was slowly added TiCl₄ (1.2 equiv.). The reaction mixture was initially stirred at 0 °C for 0.5 h and then at reflux temperature for 12 h. After complete consumption of the ketone substrate (monitored by TLC), the reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ and the combined organics were washed with water and dried over anhydrous Na₂SO₄. After removal of the organic solvent under vacuum, the residue was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired imine. The product can be further purified by recrystallization from ethanol. Substrates 1d-1n were prepared through method B.

**Method C for the synthesis of α, β-unsaturated ketoimines.**

To a stirred mixture of the ketones (15 mmol) and anhydrous ethanol (75 mmol), sulfurous oxychloride (25 mmol) was added. When the solution turned deep red, saturation Na₂CO₃ was added and the mixture was extracted twice with ether (20 mL). The organic layer was separated and dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/acetone (95/5) as the eluent, giving the pure dypnone.³

To a mixture of dypnone, methanesulfonamide (1 equiv.) and Et₃N (2.4 equiv.) in CH₂Cl₂ at 0 °C, was slowly added TiCl₄ (1.2 equiv.). The reaction mixture was initially stirred at 0 °C for 0.5 h and then at reflux temperature for 12 h. After complete consumption of the ketone substrate (monitored by TLC), the reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted.
with CH$_2$Cl$_2$ and the combined organics were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the organic solvent under vacuum, the residue was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired imine.$^{[9-16]}$ The product can be further purified by recrystallization from ethanol. Substrates 1a, 1b, 1c, 1p, 1q were prepared through method C.

N-(E)-1,3-diphenylbut-2-en-1-ylidene)methanesulfonamide 1a

White solid; M. P. 104-106 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 8.00-7.91 (m, 2H), 7.59 (m, 3H), 7.51-7.35 (m, 5H), 7.07 (s, 1H), 3.24 (s, 3H), 1.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 178.61, 146.11, 140.92, 136.93, 133.44, 129.66, 128.91, 128.89, 128.61, 126.37, 121.33, 42.91, 19.62. ESI-HRMS calculated for C$_{17}$H$_{17}$NO$_2$SNa$^+$ ([M+Na$^+$]): 322.0872; Found: 322.0867.

N-(E)-1,3-diphenylbut-2-en-1-ylidene)-N, N-dimethyl-methanesulfonamide 1b

Yellow solid; M. P. 132-134 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 8.01-7.89 (m, 2H), 7.63-7.53 (m, 3H), 7.46 (t, J = 7.6 Hz, 2H), 7.43 – 7.31 (m, 3H), 7.01 (d, J = 1.4 Hz, 1H), 2.95 (s, 6H), 1.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 178.80, 145.20, 141.10, 137.35, 133.13, 129.47, 128.86, 128.74, 128.59, 126.34, 121.96, 38.93, 19.54. ESI-HRMS calculated for C$_{18}$H$_{20}$N$_2$O$_2$SNa$^+$ ([M+Na$^+$]): 351.1138; Found: 351.1135.

N-(E)-1,3-diphenylbut-2-en-1-ylidene)-4-methylbenzenesulfonamide 1c
Faint yellow solid; M. P. 119-121 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.91 (dd, $J = 13.8$, 8.1 Hz, 4H), 7.62-7.52 (m, 3H), 7.47-7.35 (m, 5H), 7.32-7.24 (m, 2H), 7.06 (s, 1H), 2.42 (s, 3H), 1.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 178.43, 145.30, 143.52, 140.75, 138.29, 137.00, 133.49, 129.83, 129.42, 128.88, 128.83, 128.63, 127.48, 126.26, 121.75, 21.64, 19.33. ESI-HRMS calculated for C$_{23}$H$_{21}$NO$_2$SNa$^+$ ([M+Na]$^+$): 398.1185; Found: 398.1185.

N-($E$)-1-(4-fluorophenyl)-3-phenylbut-2-en-1-ylidene) methanesulfonamide 1d

Faint yellow solid; M. P. 106-108 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.99 (dd, $J = 8.7$, 5.6 Hz, 2H), 7.63-7.55 (m, 2H), 7.45-7.35 (m, 3H), 7.20-7.11 (m, 2H), 7.05 - 6.98 (m, 1H), 3.24 (s, 3H), 1.98-1.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 177.19, 166.17 (d, $J = 254$ Hz), 145.89, 140.71, 132.99, 132.30 (d, $J = 10$ Hz), 128.96, 128.65, 126.33, 121.04, 116.19 (d, $J = 22$ Hz), 42.88, 19.56. ESI-HRMS calculated for C$_{17}$H$_{16}$FNO$_2$SNa$^+$ ([M+Na]$^+$): 340.0778; Found: 340.0774.

N-($E$)-1-(4-chlorophenyl)-3-phenylbut-2-en-1-ylidene) methanesulfonamide 1e

Brown solid; M. P. 105-107 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.90 (d, $J = 8.4$ Hz, 2H), 7.63-7.53 (m, 2H), 7.48-7.36 (m, 5H), 7.05-6.99 (m, 1H), 3.24 (s, 3H), 1.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 177.29, 146.29, 140.66, 140.02, 135.28, 130.96, 129.28, 129.03, 128.66, 126.34, 120.85, 42.89, 19.65. ESI-HRMS calculated for C$_{17}$H$_{16}$ClNO$_2$SNa$^+$ ([M+Na]$^+$): 356.0474; Found: 356.0482.
N-(E)-1-(4-methoxyphenyl)-3-phenylbut-2-en-1-ylidene)methanesulfonamide 1f

Yellow solid; M. P. 114-116 °C, ¹H NMR (400 MHz, CDCl₃), δ (ppm) 7.95 (d, J = 8.9 Hz, 2H), 7.63-7.55 (m, 2H), 7.43-7.32 (m, 3H), 7.01-6.92 (m, 3H), 3.89 (s, 3H), 3.21 (s, 3H), 1.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm) 177.66, 164.25, 144.57, 140.96, 132.05, 129.03, 128.68, 128.58, 126.31, 121.52, 114.27, 55.62, 42.86, 19.35. ESI-HRMS calculated for C₁₈H₁₉NO₃SNa⁺ ([M+Na]⁺): 352.0978; Found: 352.0977.

N-(E)-3-phenyl-1-(p-tolyl)but-2-en-1-ylidene)methanesulfonamide 1g

Brown solid; M. P. 96-98 °C, ¹H NMR (400 MHz, CDCl₃), δ (ppm) 7.86 (d, J = 8.0 Hz, 2H), 7.59 (dd, J = 6.0, 1.6 Hz, 2H), 7.43-7.35 (m, 3H), 7.28 (s, 2H), 7.02 (s, 1H), 3.23 (s, 3H), 2.44 (s, 3H), 1.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm) 178.45, 145.36, 144.63, 140.97, 134.10, 129.79, 129.68, 128.78, 128.59, 126.34, 121.47, 42.89, 21.79, 19.51. ESI-HRMS calculated for C₁₈H₁₉NO₂SNa⁺ ([M+Na]⁺): 336.1029; Found: 336.1025.

N-(1E)-1-(3-fluorophenyl)-3-phenylbut-2-en-1-ylidene)methanesulfonamide 1h

Yellow solid; M. P. 139-141 °C, ¹H NMR (400 MHz, CDCl₃), δ (ppm) 7.72 (m, 1H), 7.66 (m, 1H), 7.62-7.55 (m, 2H), 7.49-7.34 (m, 4H), 7.33-7.24 (m, 1H), 7.06-7.00 (m, 1H), 3.25 (s, 3H), 1.98-1.84 (m, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm) 177.24, 162.19 (d, J = 246 Hz), 146.65, 140.66, 139.14 (d, J = 7 Hz), 130.53 (d, J = 8 Hz), 129.06, 128.66, 126.37, 125.66 (d, J = 4 Hz), 120.80, 120.39 (d, J = 22 Hz), 115.95 (d, J = 23 Hz), 42.90, 19.68. ESI-HRMS calculated for C₁₇H₁₆FNO₂SNa⁺ ([M+Na]⁺):
N-(E)-1-(3-methoxyphenyl)-3-phenylbut-2-en-1-ylidene)methanesulfonamide 1i

Yellow solid; M. P. 106-108 °C, $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.58 (m, 2H), 7.54-7.46 (m, 2H), 7.44-7.33 (m, 4H), 7.17-7.10 (m, 1H), 7.05 (s, 1H), 3.86 (s, 3H), 3.24 (s, 3H), 1.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 178.49, 159.92, 146.18, 140.93, 138.33, 129.90, 128.89, 128.61, 126.37, 122.63, 121.38, 119.47, 113.85, 55.52, 42.91, 19.61. ESI-HRMS calculated for C$_{18}$H$_{19}$NO$_3$SNa$^+$ ([M+Na$^+$]): 352.0978; Found: 352.0976.

N-(E)-1-([1,1'-biphenyl]-2-yl)-3-phenylbut-2-en-1-ylidene)methanesulfonamide 1j

White solid; M. P. 103-105 °C, $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 8.03 (d, $J = 8.1$ Hz, 2H), 7.73 - 7.67 (m, 2H), 7.67 - 7.58 (m, 4H), 7.49 (t, $J = 7.4$ Hz, 2H), 7.45 - 7.34 (m, 4H), 7.08 (s, 1H), 3.26 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 178.18, 146.23, 145.78, 140.91, 139.66, 135.59, 130.28, 129.06, 128.88, 128.63, 128.46, 127.52, 127.29, 126.38, 121.34, 42.93, 19.66. ESI-HRMS calculated for C$_{23}$H$_{21}$NO$_3$SNa$^+$ ([M+Na$^+$]): 398.1185; Found: 398.1180.

N-(E)-1-phenyl-3-(p-tolyl)but-2-en-1-ylidene)methanesulfonamide 1k

Yellow solid; M. P. 119-121 °C, $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.93 (d, $J = 7.7$ Hz, 2H), 7.58 (m, 1H), 7.47 (m, 4H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.08 (s, 1H), 3.23 (s, 3H), 2.38 (s, 3H), 1.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 178.76, 146.52,
139.06, 138.01, 137.20, 129.66, 129.29, 128.88, 126.28, 120.53, 42.91, 21.26, 19.66. ESI-HRMS calculated for C$_{18}$H$_{20}$NO$_2$S$^+$ ([M+H]$^+$): 314.1202; Found: 314.1209.

N-(E)-3-(4-chlorophenyl)-1-phenylbut-2-en-1 ylidene)methanesulfonamide \textbf{II}

Yellow solid; M. P. 126-128 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.94 (d, $J = 7.7$ Hz, 2H), 7.60 (m, 1H), 7.55 - 7.44 (m, 4H), 7.41 - 7.33 (m, 2H), 7.01 (s, 1H), 3.25 (s, 3H), 1.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 178.23, 144.42, 139.34, 136.62, 134.77, 133.59, 129.62, 128.96, 128.76, 127.68, 121.71, 42.90, 19.46. ESI-HRMS calculated for C$_{17}$H$_{17}$ClNO$_2$S$^+$ ([M+H]$^+$): 334.0658; Found: 334.0663.

N-(E)-3-(naphthalen-2-yl)-1-phenylbut-2-en-1 ylidene)methanesulfonamide \textbf{1m}

Brown solid; M. P. 135-137 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 8.05-7.94 (m, 3H), 7.86 (m, 3H), 7.75 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.55-7.44 (m, 4H), 7.22 (s, 1H), 3.26 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 178.59, 145.96, 138.08, 136.98, 133.46, 133.18, 129.69, 128.94, 128.54, 128.29, 127.63, 126.62, 126.48, 125.77, 124.09, 121.80, 42.92, 19.69. ESI-HRMS calculated for C$_{21}$H$_{20}$NO$_2$S$^+$ ([M+H]$^+$): 350.1204; Found: 350.1209.

N-(E)-3-(furan-2-yl)-1-phenylbut-2-en-1 ylidene)methanesulfonamide \textbf{1n}

Red solid; M. P. 98-100 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.85 (d, $J = 7.8$ Hz, 2H), 7.57 (m, 1H), 7.50 (d, $J = 1.8$ Hz, 1H), 7.49 - 7.36 (m, 3H), 6.67 - 6.52 (m,
1H), 6.46 (dd, $J = 3.5, 1.8$ Hz, 1H), 3.23 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 177.78, 153.79, 144.22, 137.84, 136.25, 133.08, 129.61, 128.81, 117.65, 112.02, 110.97, 42.99, 17.08. ESI-HRMS calculated for C$_{15}$H$_{16}$NO$_3$S$^+$ ([M+H]$^+$): 290.0841; Found: 290.0845.

N-(3-methyl-1-phenylbut-2-en-1-ylidene)methanesulfonamide 1o

Yellow solid; M. P. 102-104 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.83 (d, $J = 7.7$ Hz, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 6.63 (s, 1H), 3.20 (s, 3H), 2.01 (d, $J = 1.3$ Hz, 3H), 1.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 178.60, 148.81, 137.64, 132.99, 129.62, 128.73, 120.40, 43.03, 26.64, 22.13. ESI-HRMS calculated for C$_{12}$H$_{16}$NO$_2$S$^+$ ([M+H]$^+$): 238.0894; Found: 238.0896.

N-(E)-1,3-diphenylallylidene)methanesulfonamide 1p

White solid; M. P. 97-99 °C, $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.94 (d, $J = 16.1$ Hz, 1H), 7.70 (d, $J = 7.6$ Hz, 2H), 7.57 (m, 3H), 7.49 (m, 2H), 7.45-7.36 (m, 3H), 7.08 (d, $J = 16.0$ Hz, 1H), 3.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 177.98, 149.23, 137.09, 134.40, 132.08, 131.25, 130.13, 129.06, 128.87, 128.54, 122.34, 43.27. ESI-HRMS calculated for C$_{16}$H$_{16}$NO$_2$S$^+$ ([M+H]$^+$): 286.0889; Found: 286.0896.

N-((E)-1,3-diphenylallylidene)-4-methylbenzenesulfonamide 1q
Yellow solid; M. P. 116-118 °C, $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 8.09 (s, 1H), 7.93 (d, $J = 7.7$ Hz, 2H), 7.65 (d, $J = 7.5$ Hz, 2H), 7.61 – 7.50 (m, 3H), 7.49 – 7.36 (m, 5H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 16.1$ Hz, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 148.92, 143.50, 138.71, 134.57, 131.14, 130.26, 129.48, 129.07, 128.78, 128.39, 127.23, 21.62. The characterization data of compound 1q is in accordance with the reported data in the literature.\[^{17}\]

III. General procedure for asymmetric hydrogenation of $\alpha,\beta$-unsaturated ketoimines

A stock solution was made by mixing Ni(OAc)$_2$ (8.8 mg, 0.05 mmol) with (S, S)-Ph-BPE (27.9 mg, 0.055 mmol) in a 1:1.1 molar ratio in anhydrous MeOH (1 mL) at room temperature overnight in a nitrogen-filled glovebox. An aliquot of the catalyst solution (0.1 mL, 0.005 mmol) was transferred by syringe into the vials charged with different substrates (0.1 mmol for each). The vials were subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H$_2$ (80 atm) at room temperature for 24 h. The hydrogen gas was released slowly and carefully. The solution was concentrated and passed through a short column of silica gel (eluent: EtOAc) to remove the metal complex. The ee values of all compounds 2 were determined by HPLC analysis on a chiral stationary phase.

(E)-N-(1,3-diphenyl-1$\lambda^3$-but-2-en-1-yl)methanesulfonamide 2a

![Chemical structure](image)

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 29.9 mg, 99% yield; 98% ee; $[\alpha]_D^{20}$ = -5.3 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R$ = 14.0 min (minor), $t_R$ = 15.7 min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.44 (d, $J = 7.0$ Hz, 2H), 7.38 (m, 4H), 7.36 - 7.27 (m, 4H), 5.89 (dd, $J = 9.1, 1.6$ Hz, 1H).
Hz, 1H), 5.51 (dd, J = 9.1, 6.2 Hz, 1H), 4.83 (d, J = 6.1 Hz, 1H), 2.76 (s, 3H), 2.22 (d, J = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 142.31, 140.44, 139.07, 129.09, 128.46, 128.15, 127.80, 127.03, 126.76, 125.92, 56.14, 42.33, 16.60. ESI-HRMS calculated for C$_{17}$H$_{19}$NO$_2$SNa$^+$ ([M+Na]$^+$): 324.1029; Found: 324.1022.

(E)-N-(1,3-diphenyl-1λ$^3$-but-2-en-1-yl)-N,N-dimethyl-methanesulfonamide 2b

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 32.0 mg, 97% yield; 97% ee; [α]$_{D}^{20}$ = -13.5 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 254 nm; t$_R$ = 23.1 min (minor), t$_R$ = 25.6 min (major). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.45 - 7.40 (m, 2H), 7.38 (m, 4H), 7.31 (m, 4H), 5.88 (m, 1H), 5.36 (dd, J = 9.2, 5.5 Hz, 1H), 4.67 (d, J = 5.6 Hz, 1H), 2.63 (s, 6H), 2.19 (d, J = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 142.56, 141.34, 138.02, 128.88, 128.40, 127.89, 127.61, 127.59, 127.02, 125.93, 56.44, 37.62, 16.54. ESI-HRMS calculated for C$_{18}$H$_{22}$N$_2$O$_2$SNa$^+$ ([M+Na]$^+$): 353.1294; Found: 353.1289.

(E)-N-(1,3-diphenyl-1λ$^3$-but-2-en-1-yl)-4-methylbenzenesulfonamide 2c

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 37.5 mg, 99% yield; 97% ee; [α]$_{D}^{20}$ = -35.4 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t$_R$ = 19.7 min (major), t$_R$ = 22.5 min (minor). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.67 (d, J = 8.3 Hz, 2H), 7.32 - 7.21 (m, 8H), 7.17 (d, J = 8.0 Hz, 2H), 7.10 (dd, J = 7.6, 2.0 Hz, 2H), 5.58 (dd, J = 9.1, 1.5 Hz, 1H), 5.35 (dd, J = 9.2, 6.6 Hz,
1H), 4.95 (d, J = 6.6 Hz, 1H), 2.34 (s, 3H), 1.97 (d, J = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 143.29, 142.36, 140.13, 137.95, 137.90, 129.47, 128.76, 128.15, 127.79, 127.46, 127.28, 126.93, 126.89, 125.83, 56.08, 21.49, 16.31. ESI-HRMS calculated for C$_{23}$H$_{23}$NO$_2$SNa$^+$ ([M+Na]$^+$): 400.1342; Found: 400.1337.

(E)-N-(1-(4-fluorophenyl)-3-phenyl-1λ$_3$-but-2-en-1-yl)methanesulfonamide 2d

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 31.7 mg, 99% yield; 98% ee; [α]$_D^{20}$ = -7.5 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t$_R$ = 12.3 min (minor), t$_R$ = 17.4 min (major). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.45 - 7.26 (m, 7H), 7.10 - 7.02 (m, 2H), 5.86 (dd, J = 9.1, 1.4 Hz, 1H), 5.49 (dd, J = 9.2, 6.4 Hz, 1H), 5.00 (d, J = 6.4 Hz, 1H), 2.77 (s, 3H), 2.20 (d, J = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) 162.29 (d, J = 246 Hz), 142.07, 139.10, 136.23 (d, J = 3 Hz), 128.68 (d, J = 8 Hz), 128.43, 127.83, 126.42, 125.83, 115.86 (d, J = 22 Hz), 55.37, 42.22, 16.51. ESI-HRMS calculated for C$_{17}$H$_{18}$FNO$_2$SNa$^+$ ([M+Na]$^+$): 342.0934; Found: 342.0929.

(E)-N-(1-(4-chlorophenyl)-3-phenyl-1λ$_3$-but-2-en-1-yl)methanesulfonamide 2e

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 32.1 mg, 96% yield; 99% ee; [α]$_D^{20}$ = 10.7 (c = 1.0, MeOH); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t$_R$ = 13.0 min (minor), t$_R$ = 23.7 min (major). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm) 7.41 - 7.26 (m, 9H), 5.83 (m, 1H), 5.47 (dd, J = 9.2, 6.5 Hz, 1H), 5.08
(d, J = 6.5 Hz, 1H), 2.77 (s, 3H), 2.20 (d, J = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 142.07, 139.36, 139.07, 133.90, 129.19, 128.51, 128.46, 128.41, 127.95, 126.23, 125.91, 55.50, 42.31, 16.62. ESI-HRMS calculated for C$_{17}$H$_{18}$ClNO$_2$SNa$^+$ ([M+Na$^+$]): 358.0639; Found: 358.0631.

(E)-N-(1-(4-methoxyphenyl)-3-phenyl-1λ$^3$-but-2-en-1-yl)methanesulfonamide 2f

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 32.7 mg, 99% yield; >99% ee; $[\alpha]_D^{20} = 10.4$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R$ = 20.8 min (minor), $t_R$ = 30.5 min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.41 - 7.27 (m, 7H), 6.94 - 6.87 (m, 2H), 5.89 (m, 1H), 5.46 (dd, J = 9.1, 6.0 Hz, 1H), 4.74 (d, J = 6.0 Hz, 1H), 3.81 (s, 3H), 2.75 (s, 3H), 2.20 (d, J = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 159.36, 142.38, 138.74, 132.42, 128.44, 128.29, 127.75, 126.94, 125.90, 114.37, 55.65, 55.36, 42.34, 16.54. ESI-HRMS calculated for C$_{18}$H$_{21}$NO$_3$SNa$^+$ ([M+Na$^+$]): 354.1134; Found: 354.1130.

(E)-N-(3-phenyl-1-(p-tolyl)-1λ$^3$-but-2-en-1-yl)methanesulfonamide 2g

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 31.1 mg, 99% yield; 99% ee; $[\alpha]_D^{20} = 13.5$ (c = 1.0, MeOH); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R$ = 14.5 min (minor), $t_R$ = 22.4 min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.40 - 7.35 (m, 2H), 7.35 - 7.26 (m, 5H), 7.18 (d, J = 7.9 Hz, 2H), 5.89 (dd, J = 9.2, 1.5 Hz, 1H), 5.47 (s, 1H), 4.91 (d, J = 6.4 Hz, 1H), 2.75 (s, 3H), 2.34 (s,
$^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.41 - 7.27 (m, 6H), 7.22 (d, $J$ = 8.2 Hz, 1H), 7.15 (m, 1H), 7.01 (m, 1H), 5.83 (dd, $J$ = 9.2, 1.5 Hz, 1H), 5.52 (s, 1H), 4.87 (d, $J$ = 6.3 Hz, 1H), 2.81 (s, 3H), 2.23 (d, $J$ = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 163.02 (d, $J$ = 246 Hz), 143.06 (d, $J$ = 7 Hz), 141.99, 139.41, 130.55 (d, $J$ = 8 Hz), 128.43, 127.87, 126.03, 125.85, 122.55 (d, $J$ = 3 Hz), 114.96 (d, $J$ = 21 Hz), 113.88 (d, $J$ = 22 Hz), 55.54 (d, $J$ = 2 Hz), 42.22, 16.55. ESI-HRMS calculated for C$_{17}$H$_{18}$FNO$_2$SNa$^+$ ([M+Na]$^+$): 342.0934; Found: 342.0928.

(E)-N-(1-(3-fluorophenyl)-3-phenyl-1\(^3\)-but-2-en-1-yl)methanesulfonamide 2h

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 31.6 mg, 99% yield; >99% ee; $[^\alpha]_D^{20} = -13.8$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; UV detection at 254 nm; $t_R$ = 23.2 min (minor), $t_R$ = 24.1 min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.41 - 7.27 (m, 6H), 7.22 (d, $J$ = 8.2 Hz, 1H), 7.15 (m, 1H), 7.01 (m, 1H), 5.83 (dd, $J$ = 9.2, 1.5 Hz, 1H), 5.52 (s, 1H), 4.87 (d, $J$ = 6.3 Hz, 1H), 2.81 (s, 3H), 2.23 (d, $J$ = 1.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 163.02 (d, $J$ = 246 Hz), 143.06 (d, $J$ = 7 Hz), 141.99, 139.41, 130.55 (d, $J$ = 8 Hz), 128.43, 127.87, 126.03, 125.85, 122.55 (d, $J$ = 3 Hz), 114.96 (d, $J$ = 21 Hz), 113.88 (d, $J$ = 22 Hz), 55.54 (d, $J$ = 2 Hz), 42.22, 16.55. ESI-HRMS calculated for C$_{17}$H$_{18}$FNO$_2$SNa$^+$ ([M+Na]$^+$): 342.0934; Found: 342.0928.

(E)-N-(1-(3-methoxyphenyl)-3-phenyl-1\(^3\)-but-2-en-1-yl)methanesulfonamide 2i

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 32.8 mg, 99% yield; 99% ee; $[^\alpha]_D^{20} = 4.6$ (c = 1.0, MeOH); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R$ = 20.4 min (major), $t_R$ = 22.6 min (minor). $^1$H NMR (400 MHz,
CDCl$_3$, $\delta$ (ppm) 7.41 - 7.36 (m, 2H), 7.36 - 7.27 (m, 4H), 7.05 - 6.94 (m, 2H), 6.85 (dd, $J = 8.2$, 2.6 Hz, 1H), 5.87 (dd, $J = 9.1$, 1.5 Hz, 1H), 5.47 (dd, $J = 9.1$, 6.2 Hz, 1H), 4.81 (d, $J = 6.2$ Hz, 1H), 3.82 (s, 3H), 2.79 (s, 3H), 2.22 (d, $J = 1.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 160.08, 142.30, 142.07, 139.14, 130.16, 128.45, 127.80, 126.67, 125.92, 119.17, 113.29, 112.79, 56.09, 55.35, 42.34, 16.60.

ESI-HRMS calculated for C$_{18}$H$_{21}$NO$_3$SNa$^+$ ([M+Na]$^+$): 354.1134; Found: 354.1127.

(E)-N-(1-((1,1'-biphenyl)-2-yl)-3-phenyl-1$\lambda^3$-but-2-en-1-yl)methanesulfonamide 2j

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 37.4 mg, 99% yield; >99% ee; $[\alpha]_D^{20} = 8.2$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak OD-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R = 60.0$ min (minor), $t_R = 72.6$ min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.63 - 7.53 (m, 4H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.47 - 7.38 (m, 4H), 7.38 - 7.27 (m, 4H), 5.93 (dd, $J = 9.2$, 1.6 Hz, 1H), 5.55 (dd, $J = 9.2$, 6.5 Hz, 1H), 5.11 (d, $J = 6.5$ Hz, 1H), 2.79 (s, 3H), 2.23 (d, $J = 1.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 142.31, 140.98, 140.40, 139.49, 138.94, 128.91, 128.49, 127.83, 127.74, 127.59, 127.47, 127.11, 126.72, 125.96, 55.90, 42.34, 16.63. ESI-HRMS calculated for C$_{23}$H$_{23}$NO$_2$SNa$^+$ ([M+Na]$^+$): 400.1342; Found: 400.1337.

(E)-N-(1-phenyl-3-(p-tolyl)- 1$\lambda^3$-but-2-en-1-yl)methanesulfonamide 2k

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 29.9 mg, 95% yield; 97% ee; $[\alpha]_D^{20} = -5.2$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak OD-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min; UV
detection at 254 nm; t_R = 9.8 min (major), t_R = 30.6 min (minor). ^1H NMR (400 MHz, CDCl_3), δ (ppm) 7.43 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 8.4 Hz, 3H), 7.13 (d, J = 7.8 Hz, 2H), 5.87 (d, J = 9.1 Hz, 1H), 5.49 (dd, J = 9.2, 6.4 Hz, 1H), 4.98 (d, J = 6.4 Hz, 1H), 2.74 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H); ^13C NMR (100 MHz, CDCl_3), δ (ppm) 140.61, 139.39, 138.69, 137.64, 129.13, 129.03, 128.05, 127.04, 126.00, 125.78, 56.16, 42.24, 21.12, 16.53. ESI-HRMS calculated for C_{18}H_{21}NO_2SNa^+ ([M+Na]^+): 338.1179; Found: 338.1185.

(E)-N-(3-(4-chlorophenyl)-1-phenyl-1λ^3-butyne-2-en-1-yl)methanesulfonamide 2l

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 32.1 mg, 96% yield; 97% ee; [α]_D^20 = 0.4 (c = 1.0, CHCl_3); The enantiomeric excess was determined by HPLC on chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 14.6 min (major), t_R = 28.2 min (minor). ^1H NMR (400 MHz, CDCl_3), δ (ppm) 7.47 – 7.35 (m, 4H), 7.29 (d, J = 2.4 Hz, 5H), 5.89 (d, J = 9.1 Hz, 1H), 5.48 (dd, J = 9.1, 6.3 Hz, 1H), 5.06 (d, J = 6.3 Hz, 1H), 2.73 (s, 3H), 2.18 (s, 3H); ^13C NMR (100 MHz, CDCl_3), δ (ppm) 140.71, 140.36, 137.68, 133.55, 129.14, 128.55, 128.20, 127.31, 127.23, 126.98, 56.16, 42.26, 16.52. ESI-HRMS calculated for C_{17}H_{18}ClNO_2SNa^+ ([M+Na]^+): 358.0635; Found: 358.0639.

(E)-N-(3-(naphthalen-2-yl)-1-phenyl-1λ^3-butyne-2-en-1-yl)methanesulfonamide 2m

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; Brown solid; 32.5 mg, 92% yield; 98% ee; [α]_D^20 = 7.9 (c = 1.0, CHCl_3); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV
detection at 254 nm; $t_R = 22.6$ min (minor), $t_R = 24.4$ min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.84 – 7.75 (m, 4H), 7.53 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.50 – 7.42 (m, 4H), 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 6.03 (dd, $J = 9.1, 1.4$ Hz, 1H), 5.56 (dd, $J = 9.1, 6.4$ Hz, 1H), 5.02 (d, $J = 6.4$ Hz, 1H), 2.76 (s, 3H), 2.31 (d, $J = 1.4$ Hz, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 140.50, 139.43, 138.75, 133.29, 132.87, 129.12, 128.19, 128.16, 128.02, 127.58, 127.30, 127.05, 126.40, 126.13, 124.84, 124.07, 56.26, 42.31, 16.61. ESI-HRMS calculated for C$_{21}$H$_{21}$NO$_2$SNa$^+$ ([M+Na]$^+$): 374.1177; Found: 374.1185.

(E)-N-(3-(furan-2-yl)-1-phenyl-1$\lambda^3$-but-2-en-1-yl)methanesulfonamide 2n

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; Red solid; 25.7 mg, 88% yield; 96% ee; $[\alpha]_D^{20} = 12.4$ (c = 0.5, CHCl$_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R = 15.6$ min (minor), $t_R = 22.1$ min (major). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) 7.46 – 7.40 (m, 2H), 7.41 – 7.33 (m, 3H), 7.33 – 7.28 (m, 1H), 6.43 - 6.31 (m, 2H), 6.18 (m, 1H), 5.49 (dd, $J = 9.5, 6.1$ Hz, 1H), 4.83 (dd, $J = 6.4, 2.9$ Hz, 1H), 2.78 (s, 3H), 2.10 (d, $J = 1.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) 154.43, 142.27, 140.28, 129.08, 128.16, 127.81, 126.99, 126.94, 123.03, 111.40, 107.37, 55.57, 42.44, 13.78. ESI-HRMS calculated for C$_{15}$H$_{17}$NO$_3$SNa$^+$ ([M+Na]$^+$): 314.0853; Found: 314.0821.

N-(3-methyl-1-phenyl-1$\lambda^3$-but-2-en-1-yl)methanesulfonamide 2o

19
The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; Pale oil; 21.7 mg, 91% yield; >99% ee; [α]D²⁰ = -23.2 (c = 0.5, CHCl₃); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; tᵣ = 9.2 min (major), tᵣ = 10.0 min (minor). ¹H NMR (400 MHz, CDCl₃), δ (ppm) 7.41 - 7.32 (m, 4H), 7.30 (m, 1H), 5.40 - 5.23 (m, 2H), 4.76 (d, J = 5.2 Hz, 1H), 2.71 (s, 3H), 1.79 (dd, J = 18.1, 1.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm) 141.04, 136.77, 129.01, 128.92, 127.86, 126.87, 126.64, 124.35, 55.84, 42.16, 25.77, 18.37. ESI-HRMS calculated for C₁₂H₁₇NO₂SNa⁺ ([M+Na]⁺): 262.0866; Found: 262.0872.

(E)-N-(1,3-diphenyl-1λ³-allyl) methanesulfonamide 2p

The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 17.1 mg, 60% yield; 96% ee; [α]D²⁰ = -3.0 (c = 0.5, CHCl₃); The enantiomeric excess was determined by HPLC on chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; tᵣ = 26.0 min (major), tᵣ = 44.9 min (minor). ¹H NMR (400 MHz, CDCl₃), δ (ppm) 7.39 (dd, J = 5.6, 4.1 Hz, 5H), 7.37 - 7.26 (m, 5H), 6.62 (dd, J = 15.9, 1.3 Hz, 1H), 6.33 (dd, J = 15.8, 6.8 Hz, 1H), 5.28 (m, 1H), 5.19 – 5.01 (m, 1H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm) 139.84, 135.88, 132.51, 129.12, 129.10, 128.73, 128.53, 128.43, 128.33, 128.26, 127.21, 126.70, 126.67, 59.79, 42.29. ESI-HRMS calculated for C₁₆H₁₇NO₂SNa⁺ ([M+Na]⁺): 310.0875; Found: 310.0872.

(E)-N-(1,3-diphenyl-1λ³-allyl)-4-methylbenzenesulfonamide 2q
The title compound was purified by flash column chromatography using EA to provide desired hydrogenation product; White solid; 19.6 mg, 54% yield; 90% ee; [\(\alpha\)]\(_{D}^{20}\) = -20.6 (c = 1.0, CHCl\(_3\)); (for \(R\)-2q in Ref. 18: ([\(\alpha\)]\(_{D}^{25}\) = -31.4 (c = 1.0, CHCl\(_3\)), 95% ee for \(R\)); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; \(t_R\) = 48.9 min (major), \(t_R\) = 56.4 min (minor). \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\) (ppm) 7.71 – 7.61 (m, 2H), 7.27 – 7.22 (m, 5H), 7.21 – 7.17 (m, 2H), 7.17 – 7.14 (m, 2H), 7.13 (d, \(J = 2.0\) Hz, 1H), 6.41 – 6.28 (m, 1H), 6.07 (dd, \(J = 15.8, 6.3\) Hz, 1H), 5.15 – 5.03 (m, 2H), 2.32 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)), \(\delta\) (ppm) 143.31, 139.66, 137.73, 136.07, 132.16, 129.47, 128.75, 128.49, 128.18, 127.93, 127.90, 127.35, 127.08, 126.56, 59.80, 21.45.

IV. Gram-scale reaction

A stock solution was made by mixing Ni(OAc)\(_2\) (8.8 mg, 0.05 mmol) with (S, S)-Ph-BPE (27.9 mg, 0.055 mmol) in a 1:1.1 molar ratio in anhydrous MeOH (1 mL) at room temperature overnight in a nitrogen-filled glovebox. An aliquot of the catalyst solution (128 uL, 0.0064 mmol) was transferred by syringe into the vial charged with \(1\) (1.0 g, 3.2 mmol) in anhydrous CF\(_3\)CH\(_2\)OH (5.0 mL). The vial was subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H\(_2\) (80 atm) at 50 °C for 96 h. The hydrogen gas was released slowly and carefully. The solution was concentrated and then the residue was purified by flash column chromatography on silica gel to afford 0.95g \(2\) in 89% yield and 99% ee.
V. Reference

VI. $^1$H NMR and $^{13}$C NMR spectra
$1g$

$1h$
2m

NHMs

2n

NHMs
VII. HPLC spectra

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Acq. Method: D:\DATA\LYTH-LYH-4-656-RAC\LYTH-4-656-RAC-PURAN 2019-04-12 14-40-53\VNX-AD (1-2)-20-10-1ML-5UL-35MM-40MIN.K
Last changed: 3/13/2019 12:56:36 PM
Analysis Method: D:\METHOD\LOT\VNX-AD (1-2)-20-10-1ML-5UL-210MIN-60MIN.K
Last changed: 6/14/2019 5:14:02 PM (modified after loading)
Additional Info: Peak(s) manually integrated

Area Percent Report

---[Area Percent Report]---

Sorted By: Signal Multiplier: 1.00000
Multiplier: 1.00000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: Wavelength=254 nm
Peak RetTime Type Width Area Height Area
# [min] [min] [A450] [A59] \\
1 13.054 VV 0.2557 3.14686e+4 1458.59333 49.5630
2 24.026 BB 0.9408 3.18957e+4 475.95947 50.3370
Totals: 6.30643e+4 1934.54160

---[Instrument]---

Page 1 of 2
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Solution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: W901 A, WaveLengths=254 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.961</td>
<td>0.3235</td>
<td>346.09951</td>
<td>15.37999</td>
<td>0.7334</td>
</tr>
<tr>
<td>2</td>
<td>23.705</td>
<td>1.0823</td>
<td>4.69403e+4</td>
<td>641.92016</td>
<td>99.2766</td>
</tr>
</tbody>
</table>

Totals: 4.72904e+4 657.33615
**Data File**: D:\DATA\LUD\LUD-5-14-1\LUD-5-14-1 2019-03-13 10-06-46\010-2501.3
**Sample Name**: ZK-3-83-400E

---

**Acq. Date**: 3/24/2019 4:06:01 AM  
**Injection Date**: 3/13/2019 12:56:36 PM  
**Analysis Method**: D:\METHOD\LOT\VWD-AD [1-2]-90-20-1ML-5UL-210NM-60MIN.X  
**Last changed**: 3/13/2019 12:56:36 PM

**Additional Info**: Peak(s) manually integrated

---

**Area Percent Report**

**Sorted By**: Signal  
**Multiplier**: 1.0000  
**Solution**: 1.0000  
**Use Multiplier & Dilution Factor with ISTDs**

**Signal 1**: VWD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>Peak RefLine Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>min.</td>
<td>max.</td>
<td>[mmHg]</td>
<td>[mmHg]</td>
<td>[mmHg]</td>
</tr>
<tr>
<td>1</td>
<td>20.802</td>
<td>0.4864</td>
<td>82.80405</td>
<td>2.51315</td>
</tr>
<tr>
<td>2</td>
<td>30.510</td>
<td>1.0467</td>
<td>2.74502e4</td>
<td>307.51928</td>
</tr>
<tr>
<td><strong>Totals</strong>:</td>
<td></td>
<td></td>
<td></td>
<td>2.75410e4</td>
</tr>
</tbody>
</table>

---

**Instrument**: 6/14/2019 5:04:15 PM  
**Page 1 of 2**
Data File D:\DATA\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\005-24213
Sample Name: ZK-3-01-4Me-HAC

Acq. Operator : Seq. Line : 24
Acq. Instrument : Instrument 1 Location : Vial 85
Injection Date : 4/19/2019 4:26:15 AM Inj : 1
Inj Volume : 3.000 µl
Acq. Method : D:\DATA\LYH-4-656-RAC\LYH-4-656-RAC-FURAN 2019-04-12 14-40-53\VNL-AD (1-2)-20-10-LNL-5UL-25MIN-40MIN.X
Last changed : 3/13/2019 12:56:16 PM
Analysis Method : D:\METHOD\LOT\VNL-AD (1-2)-30-20-LNL-210MIN-60MIN.XK
Last changed : 6/14/2019 5:16:54 PM
(modified after loading)
Additional Info : Peak[s] manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.00000
Solution : 1.00000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: Wavelength=254 nm
Peak RetLine Type Width Area Height Area
μs [min] [min] [μA*sec] [μA]

| 1  | 14.536 BB | 0.3587 | 2.057098e4 | 1234.23921 | 49.8016 |
| 2  | 22.707 BB | 0.7902 | 2.950406e4 | 550.57893 | 50.1984 |

Totals : 5.87746e4 1784.85475

Instrument 1 6/14/2019 5:16:57 PM
74
Data File D:\DATA\ZL\ZL-3-91\LSL-4-31-3 2019-04-13 13-34-06\ZL-4-31-3.D
Sample Name: ZL-3-91-4101-PAK

Acq. Operator: Seq. Line: 3
Acq. Instrument: Instrument 2 Location: Vial 11
Injection Date: 4/13/2019 2:07:11 PM Inj: 1
Inj Volume: 3.000 µl

Acq. Method: D:\DATA\ZL\ZL-3-91\LSL-4-31-3 2019-04-13 13-34-06\DAD-0D-(1-2)-05-15-1XL-SUL-ALL-60MIN.X
Last changed: 4/13/2019 3:22:05 PM (modified after loading)
Analysis Method: D:\METHOD\DAD\V0D-40 (1-2)-05-20-1XL-SUL-210MIN-60MIN.X
Last changed: 6/14/2019 5:20:32 PM (modified after loading)

Additional Info: Peak(s) manually integrated

---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISDBs

Signal 1: DAD 1, Sug-254.4 Ref-off

Peak RetTime Type Width Area Height Area
# [min] [min] [nm²] [nm²] %
---|---|---|---|---|
1 50.633 BB 2.672 2.67655e+04 204.53832 49.9267
2 71.722 BB 3.3276 4.69027e+04 164.73854 50.0733

Totals: 9.06602e4 369.37696

---

Page 1 of 2
Acq. Operator:  Seq. Line:  4
Injection Date:  4/13/2019 3:30:07 PM  Inj:  1
Injection Volume:  1.000 µl
Acq. Method:  D:\DATA\ZK\ZK-01\LSL-4-31-1 2019-04-13 13-34-06\DAD-0D-(1-2)-05-15-1XL-SUL-ALL-60MIN.K
Last changed:  4/13/2019 3:30:14 PM
(modified after loading)
Analysis Method:  D:\METHOD\HPLC\HPLC-401-01-02-20-20-1XL-SUL-210NM-60MIN.K
Last changed:  6/14/2019 5:12:11 PM
(modified after loading)
Additional Info:  Peak(s) manually integrated

Sorted By:  Signal
Multiplier:  1.0000
Dilution:  1.00000
Use Multiplier & Dilution Factor with STDs

Signal 1: DAK1 B, Sig-254, 4 Ref-off

Peak Name Type Width Area Height Area
# [min] [min] [nA µFs] [nA] [%]
---- ---- -------- ------- ------- ------- -----
1 60.010 MN 1.7417 54.46716 5.21222e-1 0.1951
2 72.632 BB 3.3441 2.78585e4 97.36649 99.8049
Totals: 2.79100e4 97.09771

Instrument 1 6/14/2019 5:12:27 PM
Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISDBs

Signal 1: UVa A, Wavelength=250 nm

Peak PectTime Type Width Height Area %
# | [min] | [min] | [auFS] | [uFL] | %
---|-------|-------|--------|-------|---
1  | 22.664 | BB    | 0.5510 | 6.1041 | 64  | 1741.29834 | 49.9178 |
2  | 24.470 | BB    | 0.5812 | 6.1242 | 64  | 1645.73938 | 50.0822 |
Totals: | 1.2205e5 | 3087.03772

Instruments 1: 6/14/2019 6:29:49 PM
Sample Name: zk-3-03-timon

---

**Acq. Operator:** 17  
**Acq. Instrument:** Instrument 1  
**Location:** Vial 74  
**Inj:** 1  
**Injection Date:** 6/22/2019 10:20:12 PM  
**Inj Volume:** 3.000 μl  
**Acq. Method:** D:\DATA\ZHK\ZK\XK-2-170\XK-2-170 2019-06-12 12-33-29\ZKAD\AD(1-2)-90-10-JNL-3UL-ALL-4015N.X  
**Last changed:** 6/12/2019 9:10:29 PM (modified after loading)  
**Analysis Method:** D:\METHOD\METHOD40\[1-2]-93-7-1ML-3UL-210WX-30KX.XV  
**Last changed:** 6/13/2019 9:15:25 AM (modified after loading)  
**Additional Info:** Peak(s) manually integrated

---

**Sorted By:** Signal  
**Multiplier:** 1.00000  
**Dilution:** 1.00000  
**Use Multiplier & Dilution Factor with IS/To**

**Signal 1:** Wavelength=250 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.632</td>
<td>VV</td>
<td>0.3363</td>
<td>474.12967</td>
<td>21.59438</td>
<td>2.1534</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22.077</td>
<td>BB</td>
<td>0.5206</td>
<td>2.1543724</td>
<td>630.93332</td>
<td>97.8466</td>
<td></td>
</tr>
</tbody>
</table>

**Totals:** 2.20179e4 652.17359

---

**Instrument:** 1 6/13/2019 9:59:34 AM
NHMs

2o

Area Percent Report

Sorted By : Signal
Multiplier : 1.00000
Solution : 1.00000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: Wavelength=220 nm

Peak RetTime Type Width Area Height Area
#      [min] [min] [mmol] [mmol]
---|--------|--------|--------|--------
1 9.246 BY 0.0167 2.57242e-4 1.903.41467 39.9675
2 9.908 NM 0.1085 0.33015 1.38998 0.0324
Totals : 2.57326e-4 1984.39355
Data File D:\DATA\ZQ\ZX-9-91\ZX-9-91 2019-06-15 14-29-39\071-0401.D
Sample Name: ZX-9-91-001-HCL-RAC

+-----------------------------------------------------------------------+
| Acq. Operator :  Seq. Line :  4                                      |
| Acq. Instrument : Instrument 2 Location : Vial 71                   |
| Injection Date : 6/15/2019 4:01:36 PM Inj : 1                        |
| Inj Volume : 3.000 uL                                               |
| Acq. Method : D:\DATA\ZQ\ZX-9-91\ZX-9-91 2019-06-15 14-29-39\DAD-02 (1-2)-90-10-1ML-3UL-ALL-60MIN-0615.X |
| Last changed : 6/15/2019 3:59:12 PM                                 |
| Analysis Method : D:\DATA\ZQ\ZX-9-91\ZX-9-91 2019-06-15 14-29-39\DAD-02 (1-2)-90-10-1ML-3UL-ALL-60MIN-0615.X |
| Last changed : 6/15/2019 3:59:12 PM                                 |
| (modified after loading)                                           |
| Additional Info : Peak(s) manually integrated                       |

Area Percent Report

Sorted By : Signal
Multiplier : 1.00000
Solution : 1.00000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD B, Sing=254.4 Peakoffs, 0.00000

Peak RetTime Type Width Area Height Area
# [min] [min] [aAU%] [aAU%] [aAU%]

| 1 | 25.826 BB | 1.1543 | 5.0564 | 4.4 | 50.9132 |
| 2 | 43.606 BB | 1.2976 | 3.0670 | 4.2 | 50.0868 |

Totals : 6.12644 634.34056

Instrument 2 6/15/2019 8:44:43 PM
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAnl B, Sgn=254.4 Reps/Off

<table>
<thead>
<tr>
<th>Peak RefLine Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[max]</td>
<td>[kA0s]</td>
<td>[kA5]</td>
</tr>
<tr>
<td>1</td>
<td>36.061</td>
<td>1.750</td>
<td>2.574389e-4</td>
<td>293.03994</td>
</tr>
<tr>
<td>2</td>
<td>44.061</td>
<td>1.9559</td>
<td>552.43103</td>
<td>4.69338</td>
</tr>
</tbody>
</table>

Totals: 2.62962e4 297.59232
Data File D:\DATA\LBD\LBD-5-160-13\LBD-5-160-13 2019-07-22 08-05-06\021-0401.D
Sample Name: IRR-190722-ZX-RAC

Acq. Operator :  Seq. Line : 4
Acq. Instrument : Instrument 1 Location : Vial 31
Injection Date : 7/22/2019 9:12:03 AM Inj : 1
Inj Volume : 5.00 μl
Acq. Method : D:\DATA\LBD\LBD-5-160-13\LBD-5-160-13 2019-07-22 08-05-06\VWD-AD(1-2)-95-5-ML-5-SUL-210XN-15XN.K
Last changed : 12/25/2018 9:16:16 PM
Analysis Method : D:\METHOD\GUAN_TAOQING\VWD-AD(1-2)-95-5-ML-5-SUL-210XN-15XN.K
Last changed : 7/22/2019 2:43:02 PM
(modified after loading)
Additional Info : Peak(s) manually integrated

![Molecular Structure](image)

---

### Area Percent Report
---

**Sort By** : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

**Signal**: VWD1, Wavelength=210 nm

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>UV</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.970</td>
<td>YB</td>
<td>1.3263</td>
<td>1.047306e5</td>
</tr>
<tr>
<td>2</td>
<td>56.768</td>
<td>DD</td>
<td>1.3457</td>
<td>1.346346e5</td>
</tr>
</tbody>
</table>

**Total** : 2.69101e5 2949.65382

---

**Instrument**: 7/22/2019 2:43:16 PM
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Solution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WD1 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.948 VB</td>
<td>1.2704</td>
<td>516.34009</td>
<td>94.83651</td>
</tr>
<tr>
<td>2</td>
<td>56.437 BB</td>
<td>1.2956</td>
<td>26.1342</td>
<td>5.1349</td>
</tr>
</tbody>
</table>

Totals : 542.47420

Instrument 1 7/22/2019 2:41:13 PM